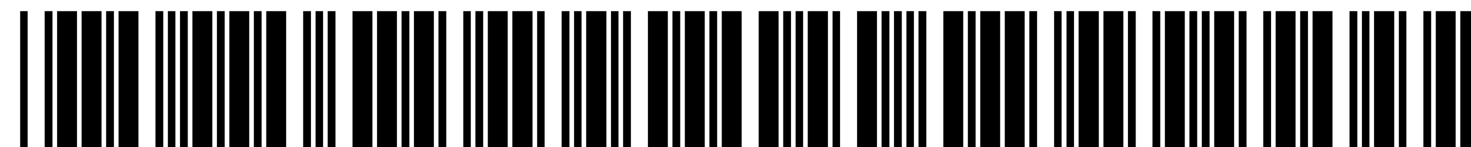

(12) **United States Patent**
Tamamori et al.

(10) **Patent No.: US 11,465,418 B2**
(45) **Date of Patent: Oct. 11, 2022**

(54) **MANUFACTURING METHOD FOR STRUCTURE AND MANUFACTURING METHOD FOR LIQUID EJECTION HEAD**

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(72) Inventors: **Kenji Tamamori**, Kanagawa (JP); **Kazuhiro Asai**, Kanagawa (JP); **Tetsushi Ishikawa**, Tokyo (JP); **Seiichiro Yaginuma**, Kanagawa (JP)

(73) Assignee: **Canon Kabushiki Kaisha**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **17/204,554**

(22) Filed: **Mar. 17, 2021**

(65) **Prior Publication Data**

US 2021/0300042 A1 Sep. 30, 2021

(30) **Foreign Application Priority Data**

Mar. 25, 2020 (JP) JP2020-054241

(51) **Int. Cl.**
B41J 2/16 (2006.01)
G03F 7/20 (2006.01)

(52) **U.S. Cl.**
CPC ***B41J 2/1631*** (2013.01); ***B41J 2/162*** (2013.01); ***G03F 7/70058*** (2013.01)

(58) **Field of Classification Search**
CPC B41J 2/1631; B41J 2/162; B41J 2/1603; B41J 2/1623; B41J 2/1628; B41J 2/1629; B41J 2/1632; B41J 2/1634; B41J 2/1635; B41J 2/1639; B41J 2/1645; G03F 7/70058; G03F 7/095; G03F 7/2022
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,451,505	B1 *	9/2002	Patel	B41C 1/1033 430/944
8,043,794	B2 *	10/2011	Noelscher	G03F 7/0035 430/311
8,728,713	B2 *	5/2014	Fabinski	G03F 7/70466 430/394
9,205,650	B2 *	12/2015	Yaginuma	B41J 2/1603

FOREIGN PATENT DOCUMENTS

JP	2017202616	A	11/2017
WO	2013-051516	A	4/2013

* cited by examiner

Primary Examiner — Hung V Nguyen
(74) *Attorney, Agent, or Firm* — Canon U.S.A., Inc., IP Division

(57) **ABSTRACT**

A manufacturing method for a structure includes preparing a dry film supported on one surface of a support; bonding the dry film to a substrate so that the dry film and the substrate are in contact with each other; performing first exposure of the dry film bonded to the substrate via the support; removing the support after the first exposure; performing second exposure of the dry film after the support is removed via a photomask; and developing the dry film after the first exposure and the second exposure.

13 Claims, 9 Drawing Sheets

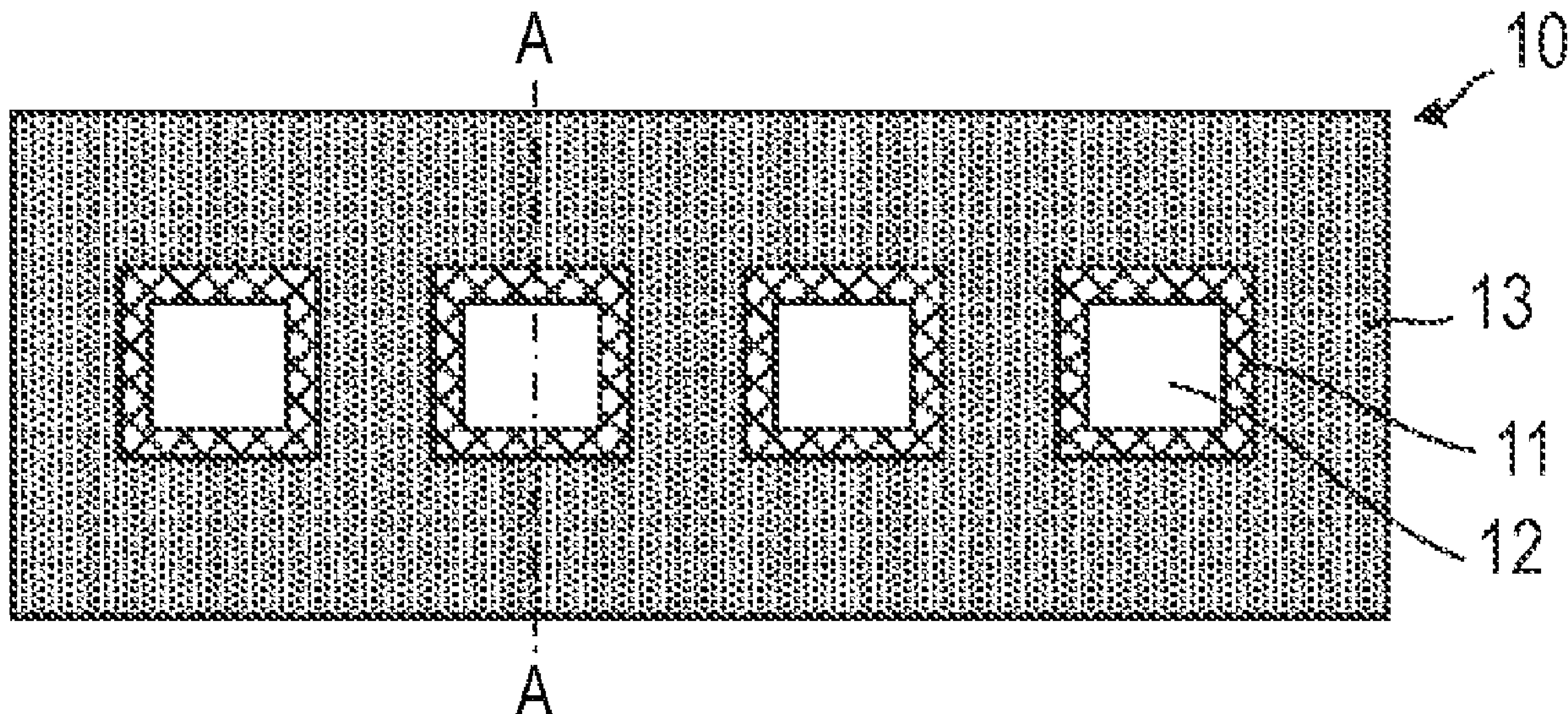


FIG. 1A

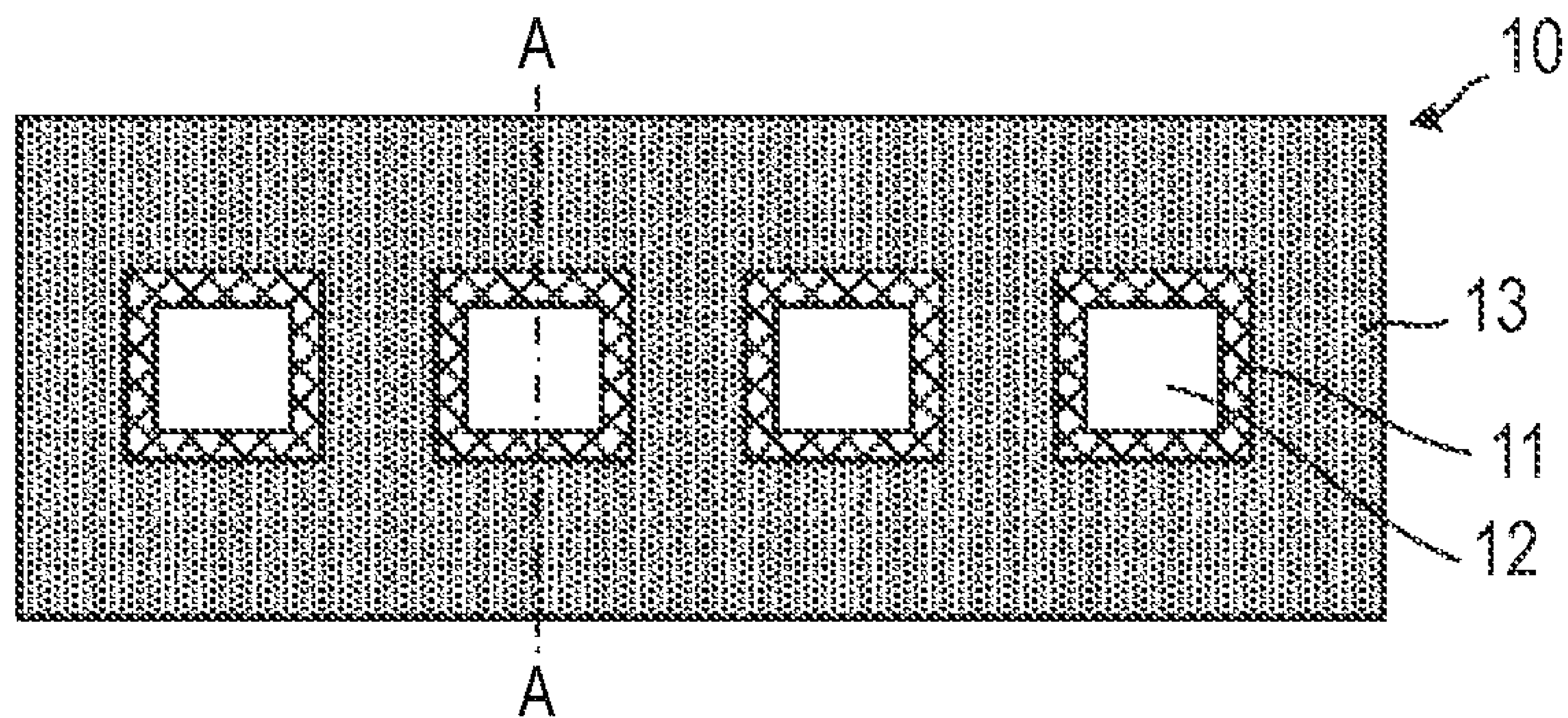


FIG. 1B

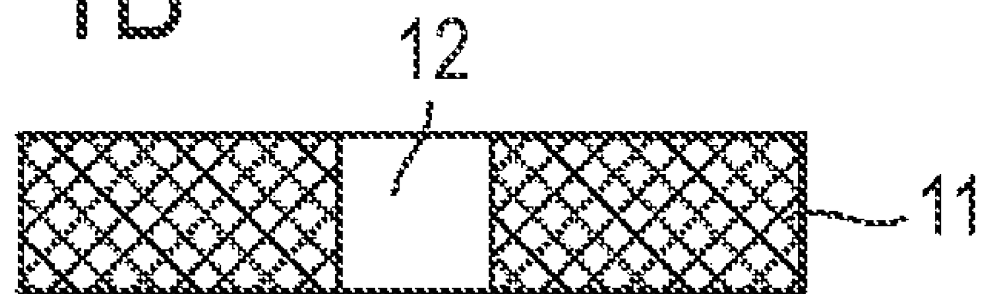


FIG. 1H

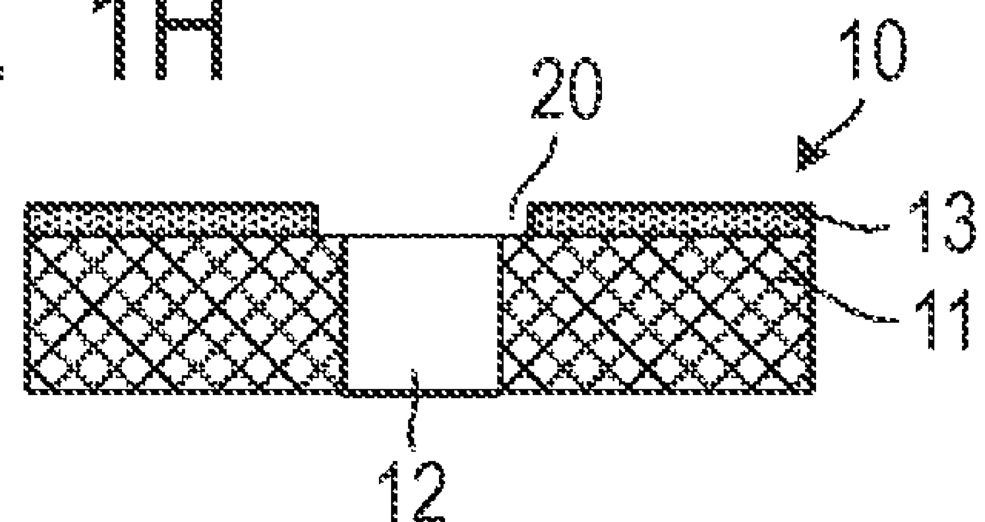


FIG. 1C

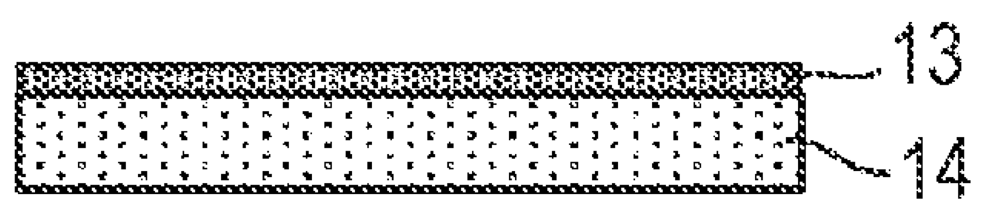


FIG. 1I

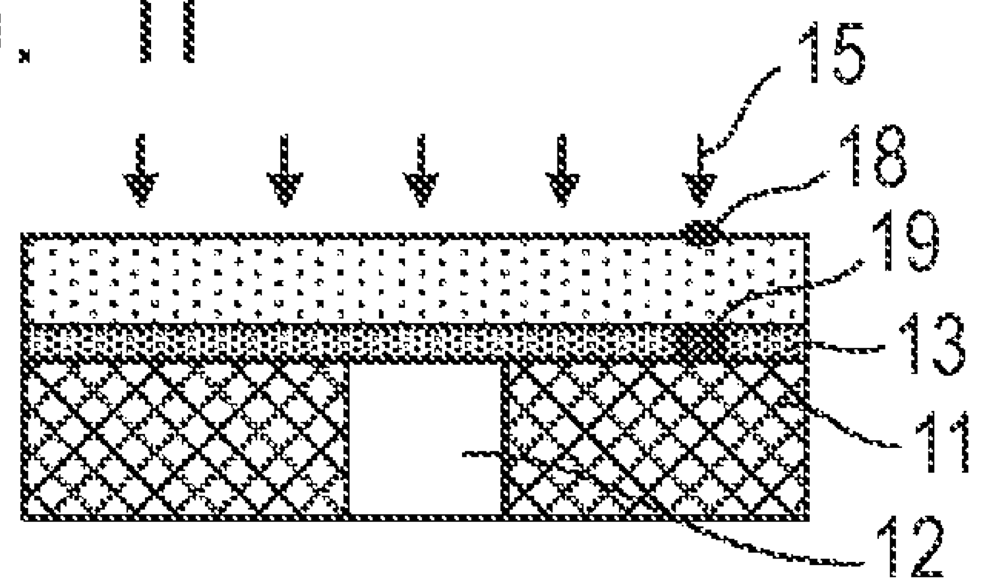


FIG. 1D

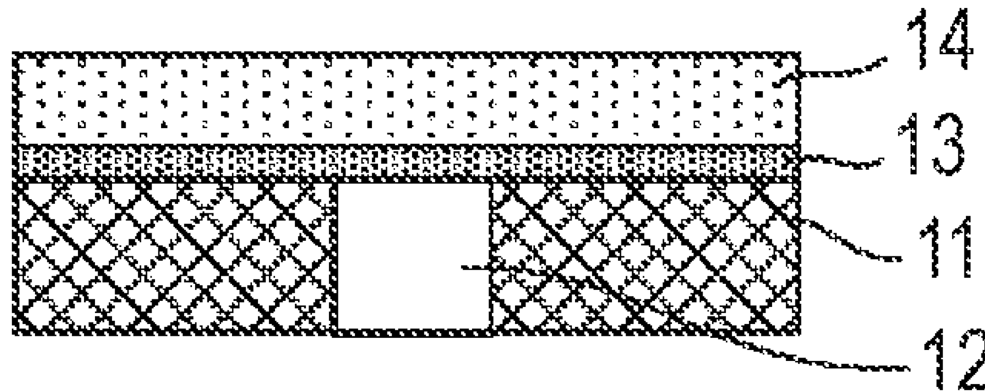


FIG. 1J

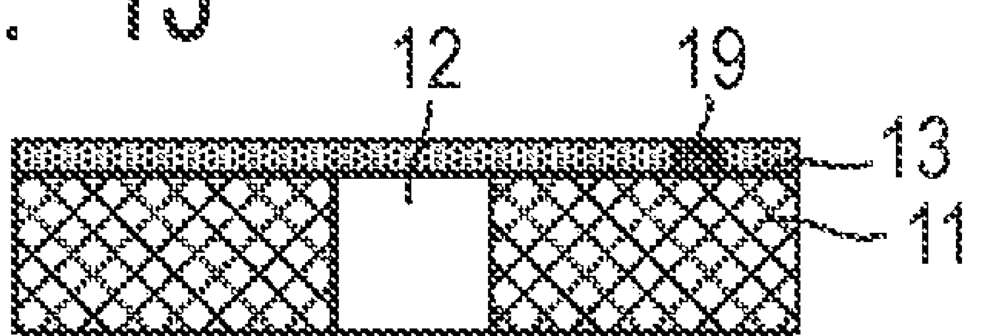


FIG. 1E

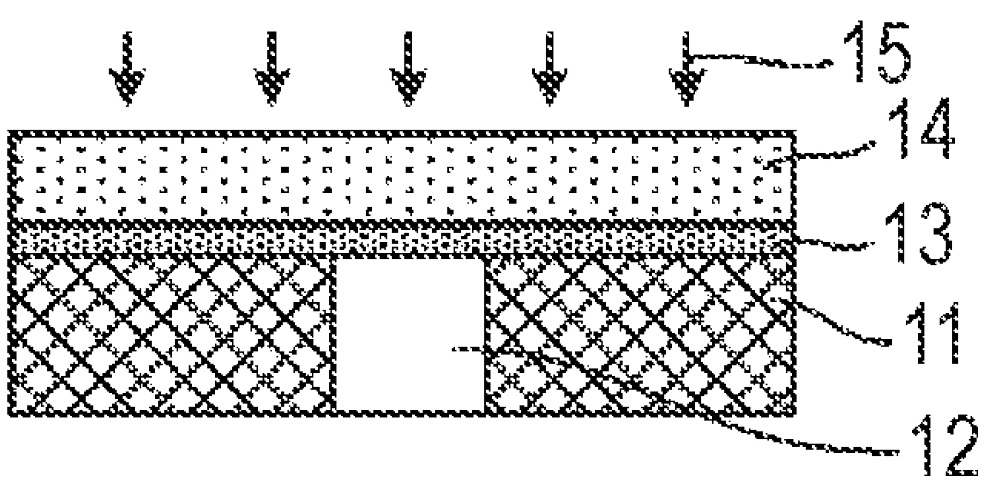


FIG. 1K

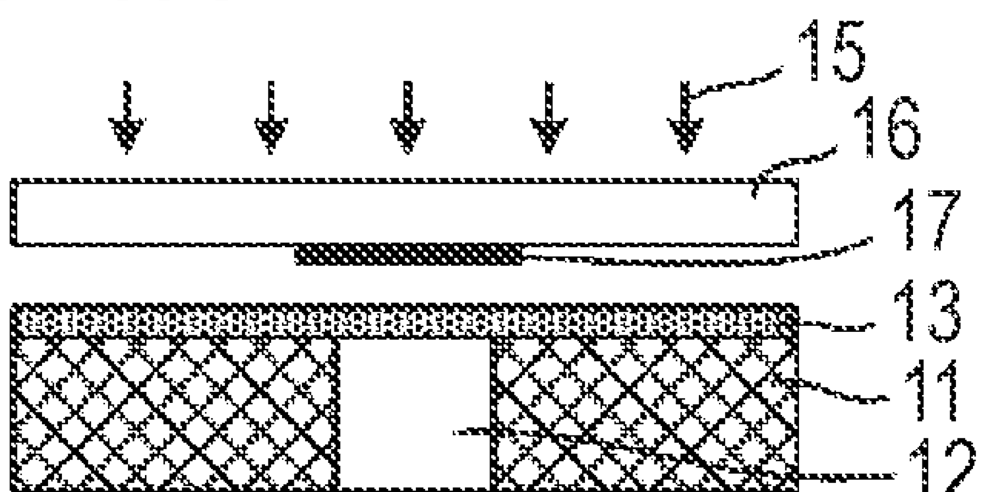


FIG. 1F

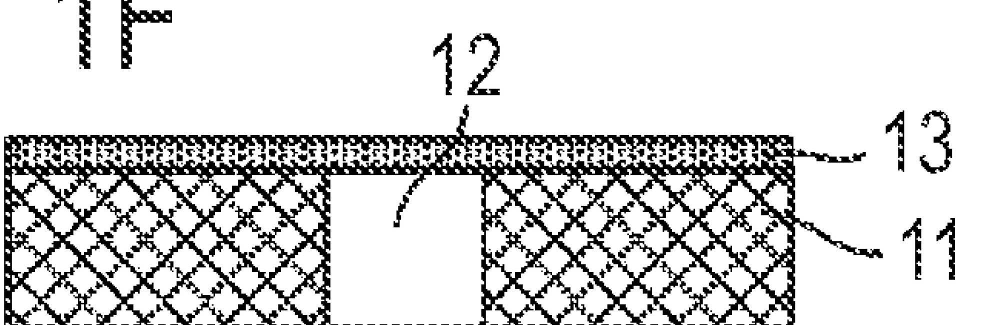


FIG. 1G

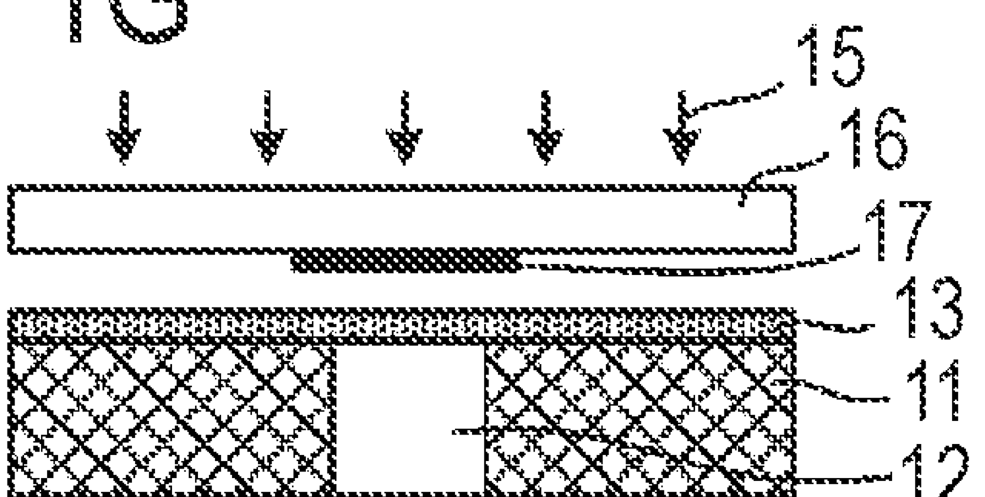


FIG. 1L

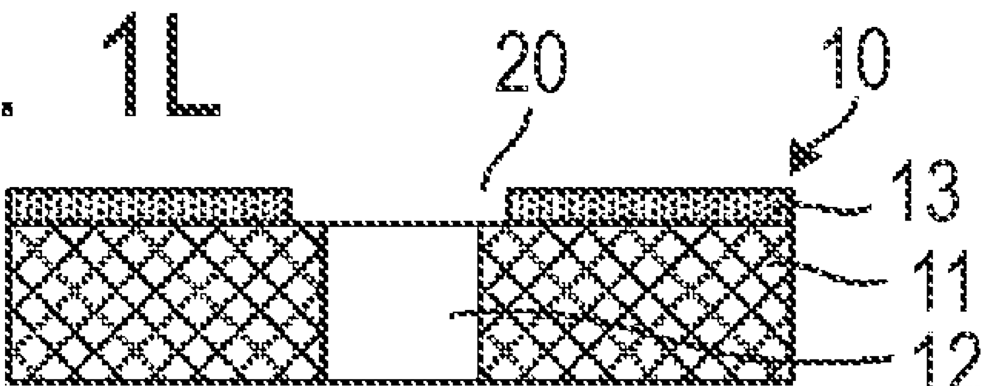


FIG. 2A

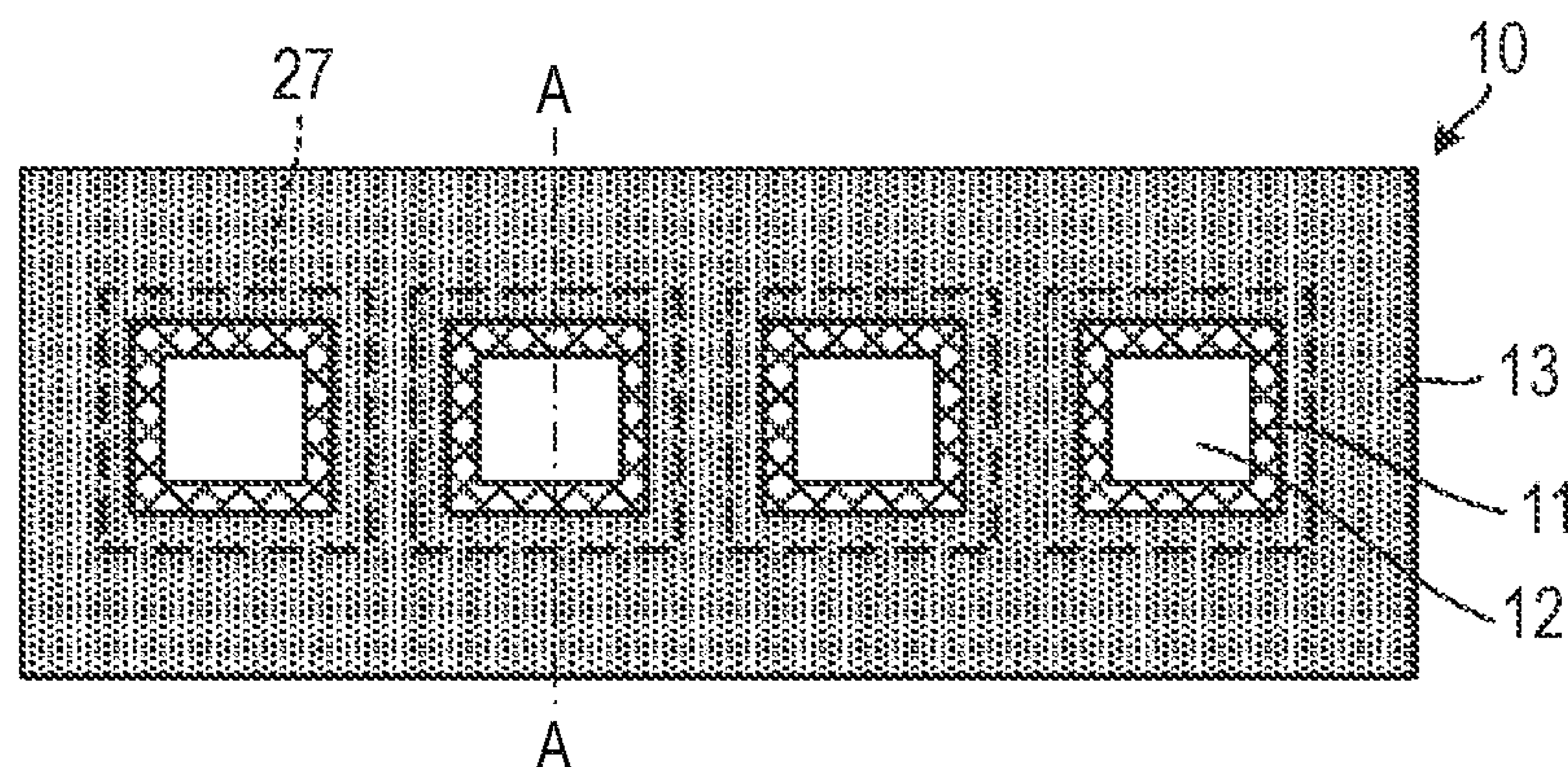


FIG. 2B

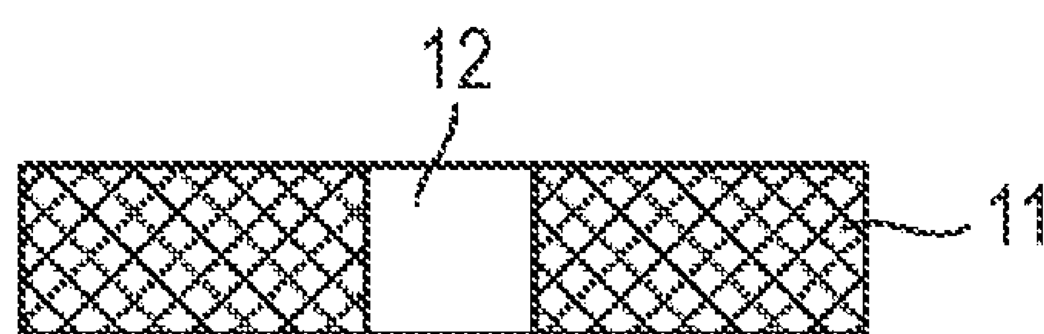


FIG. 2F

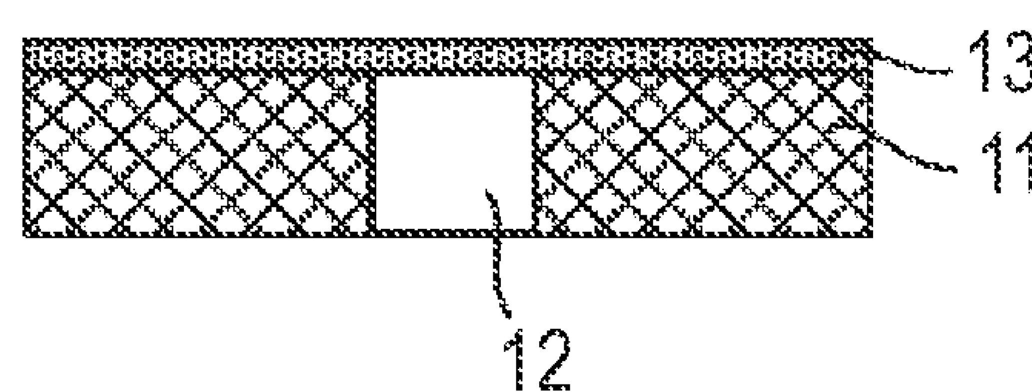


FIG. 2C

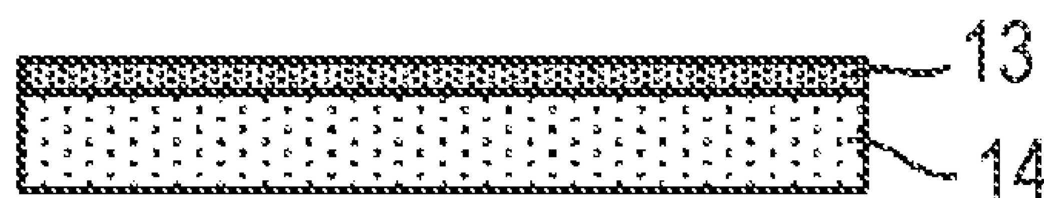


FIG. 2G

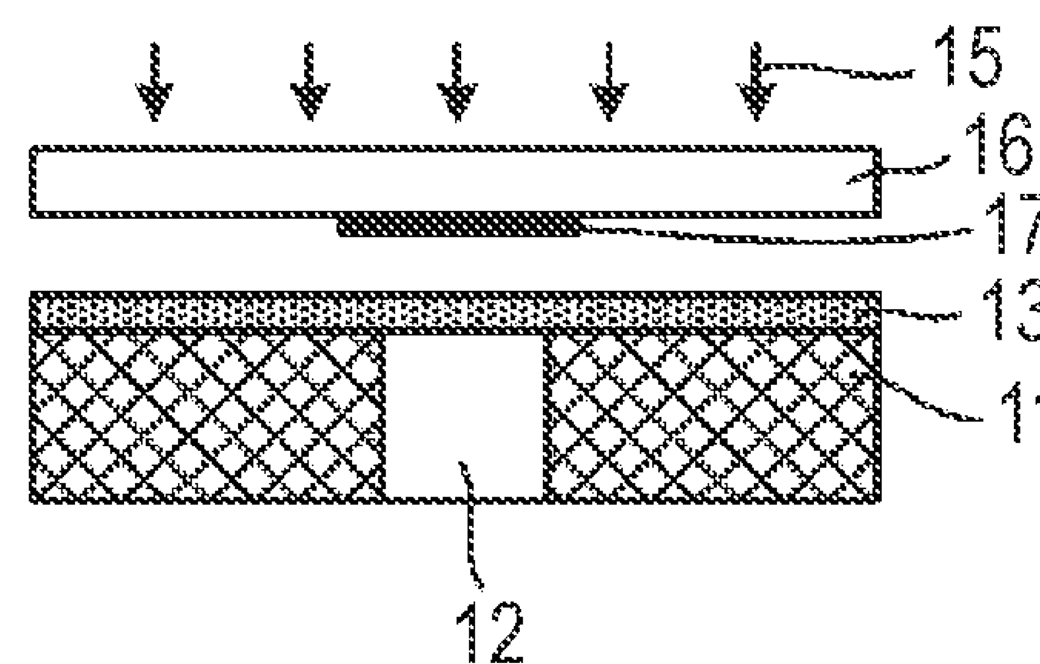


FIG. 2D

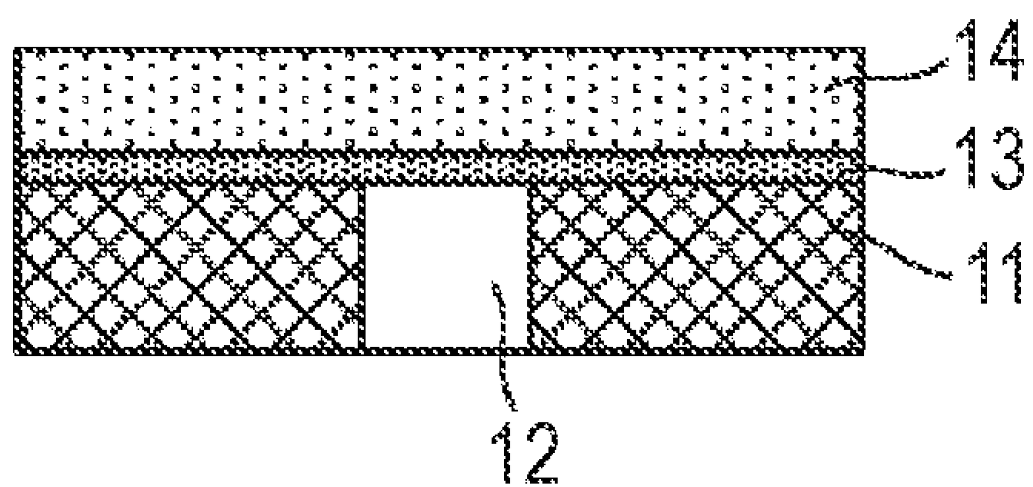


FIG. 2H

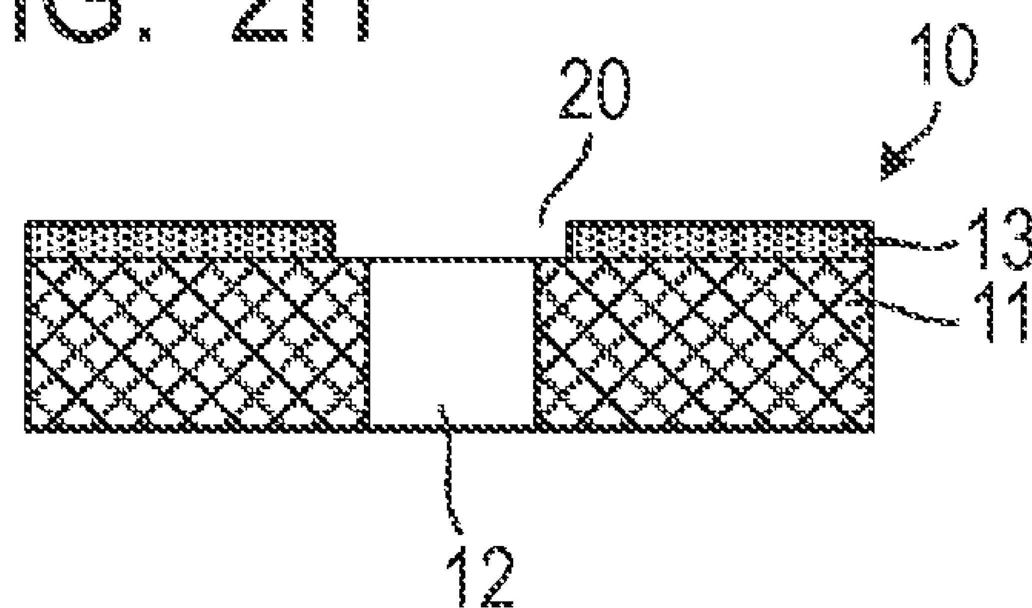
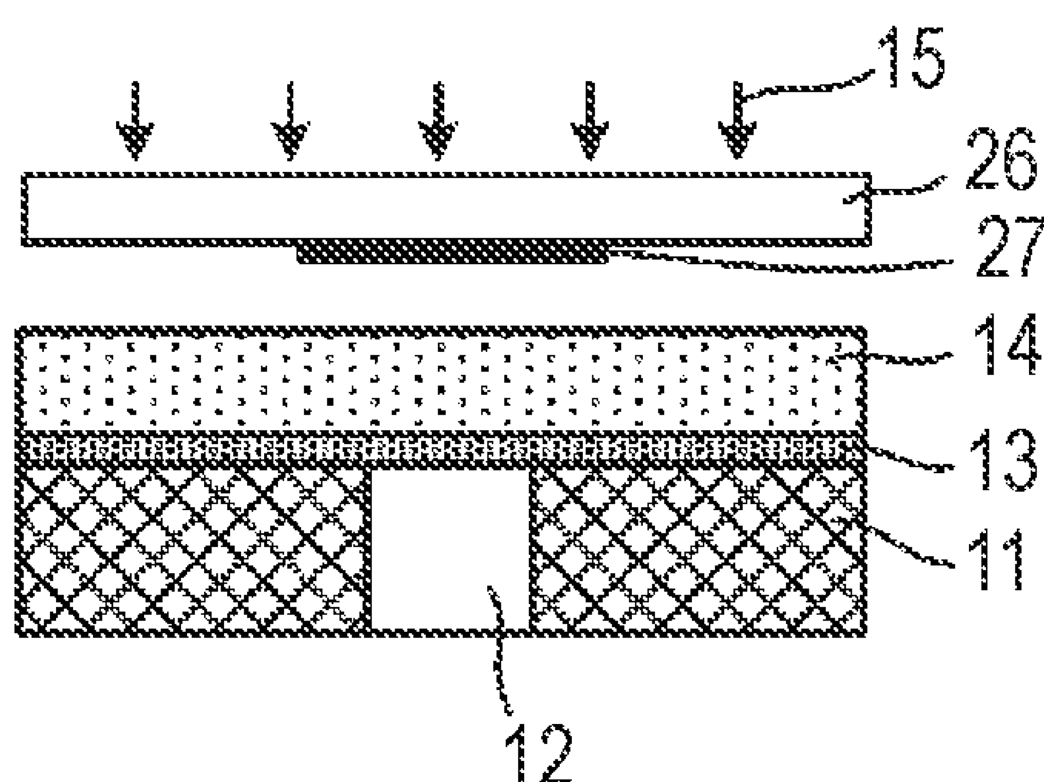


FIG. 2E



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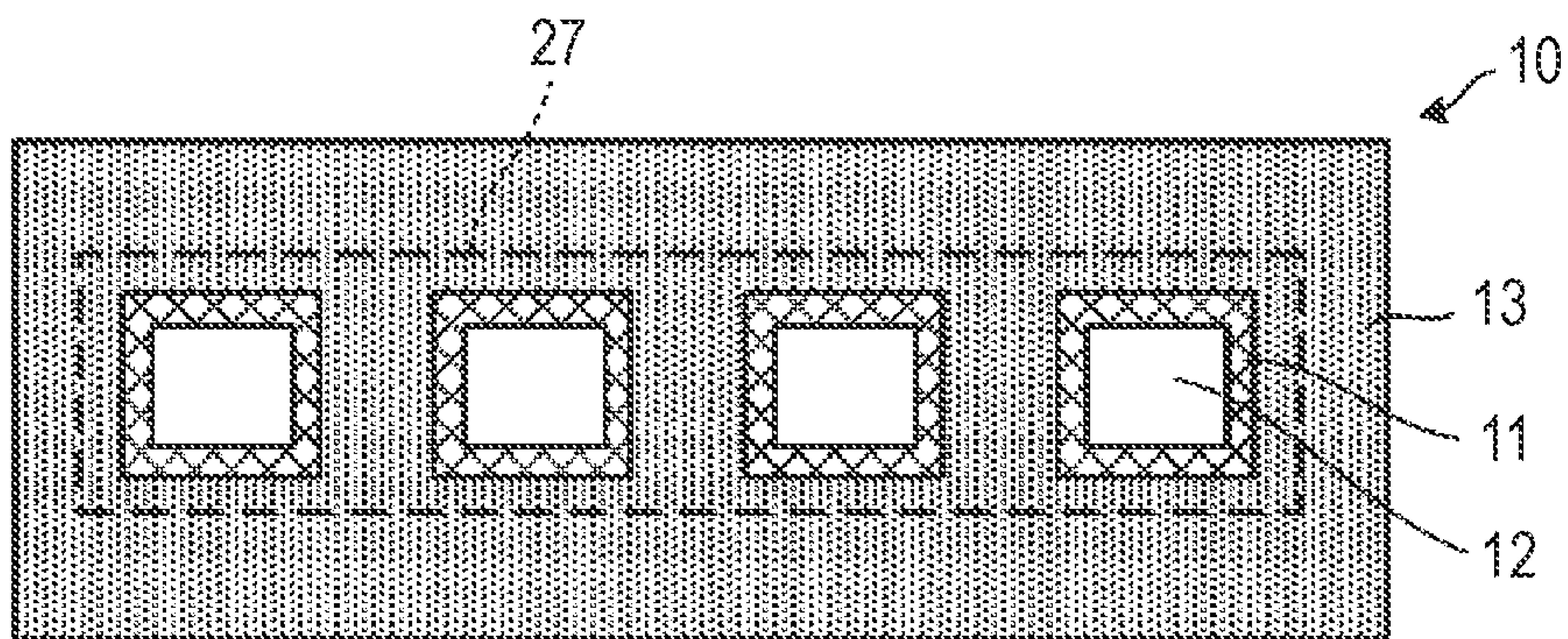


FIG. 4

FIG. 5A

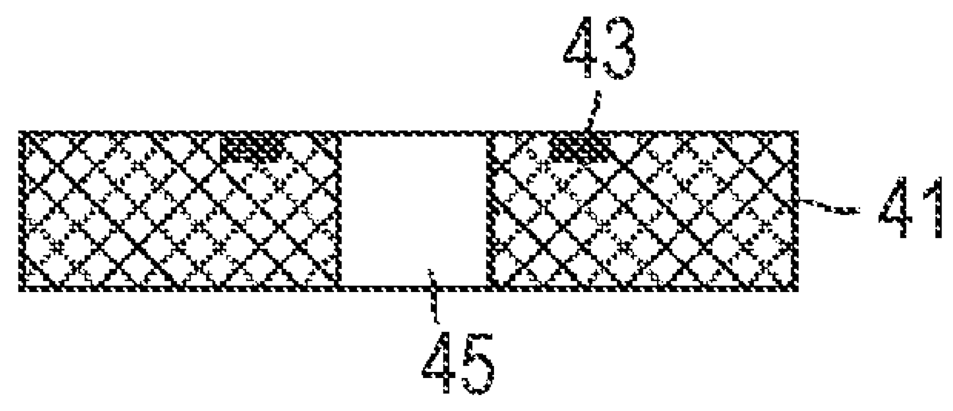


FIG. 5B

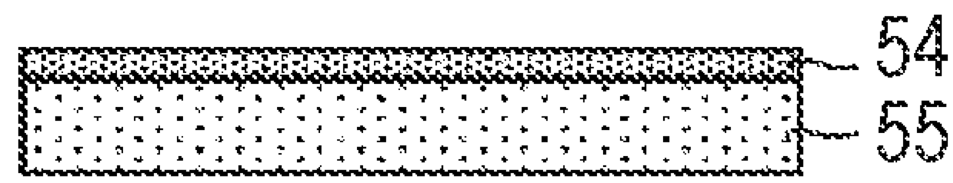


FIG. 5C

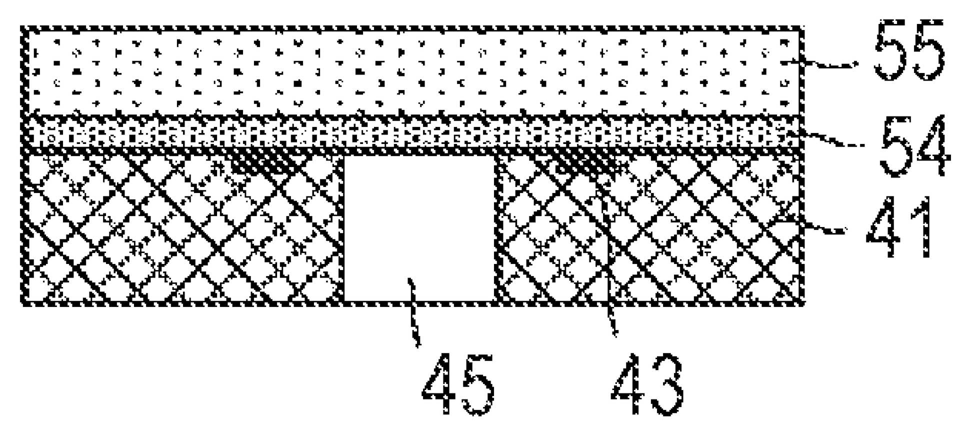


FIG. 5D

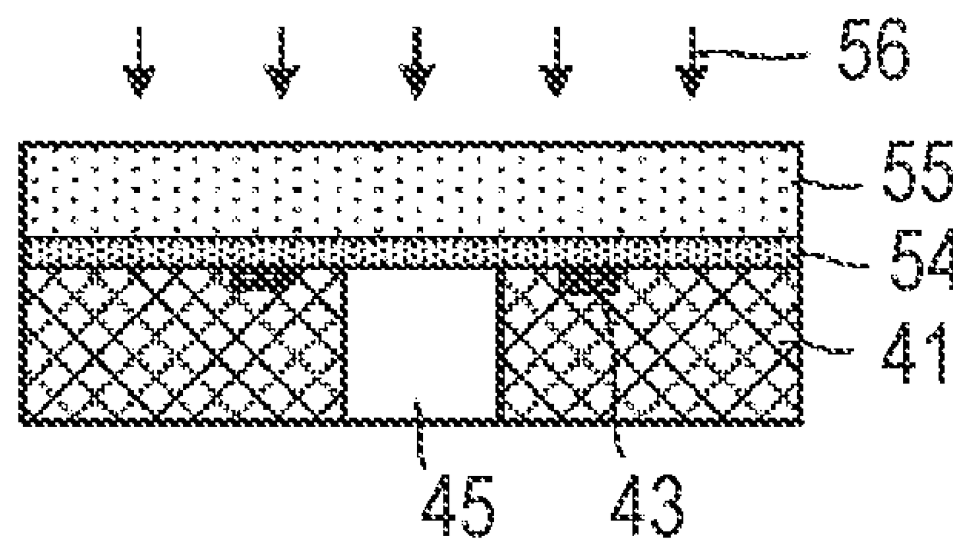


FIG. 5E

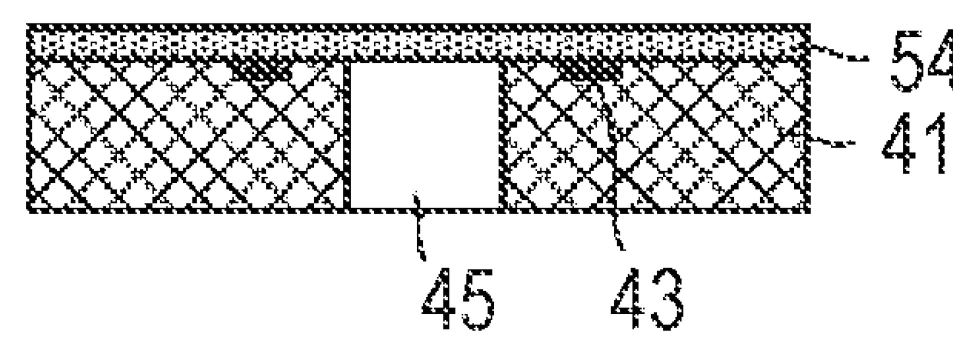


FIG. 5F

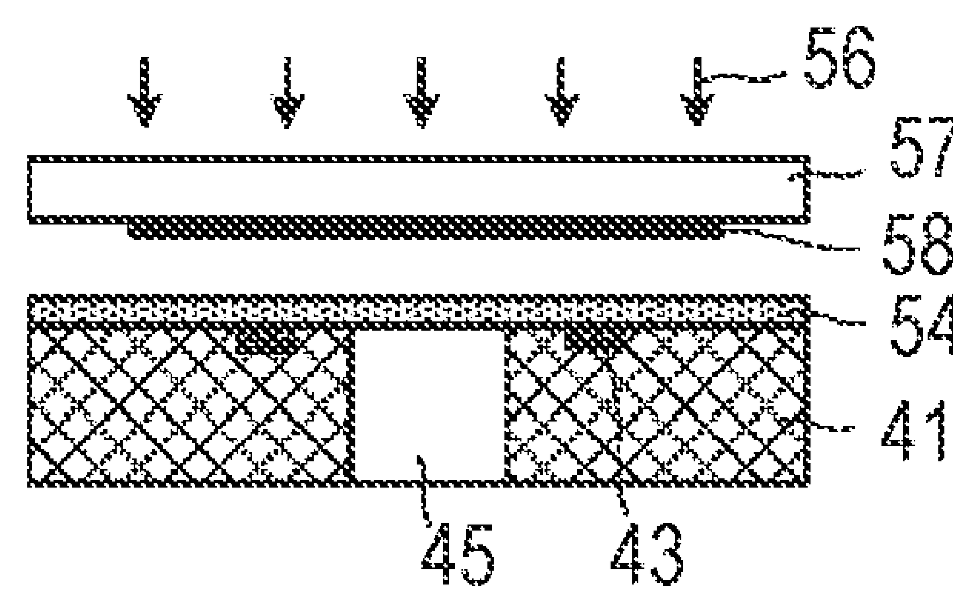


FIG. 5G

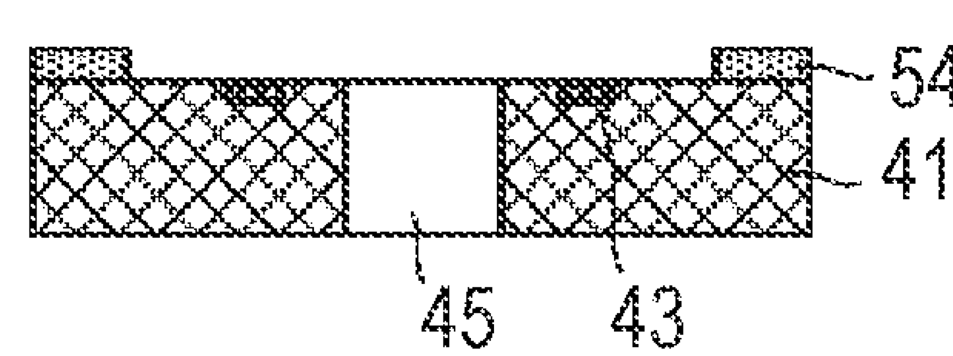


FIG. 5H

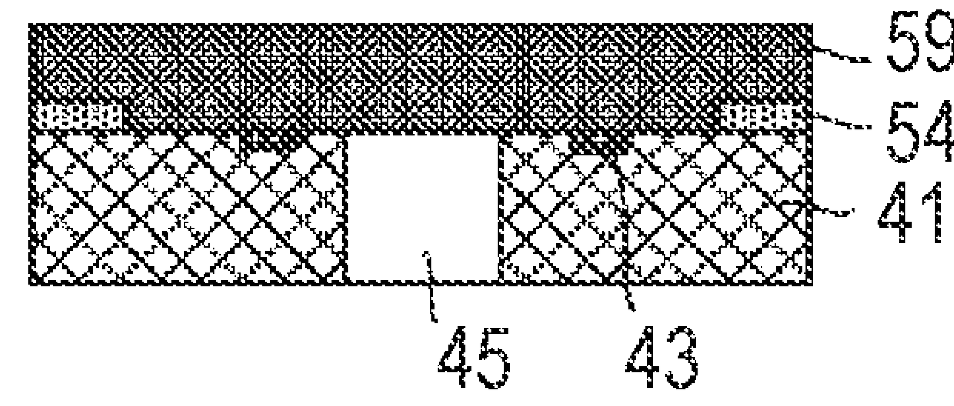


FIG. 5I

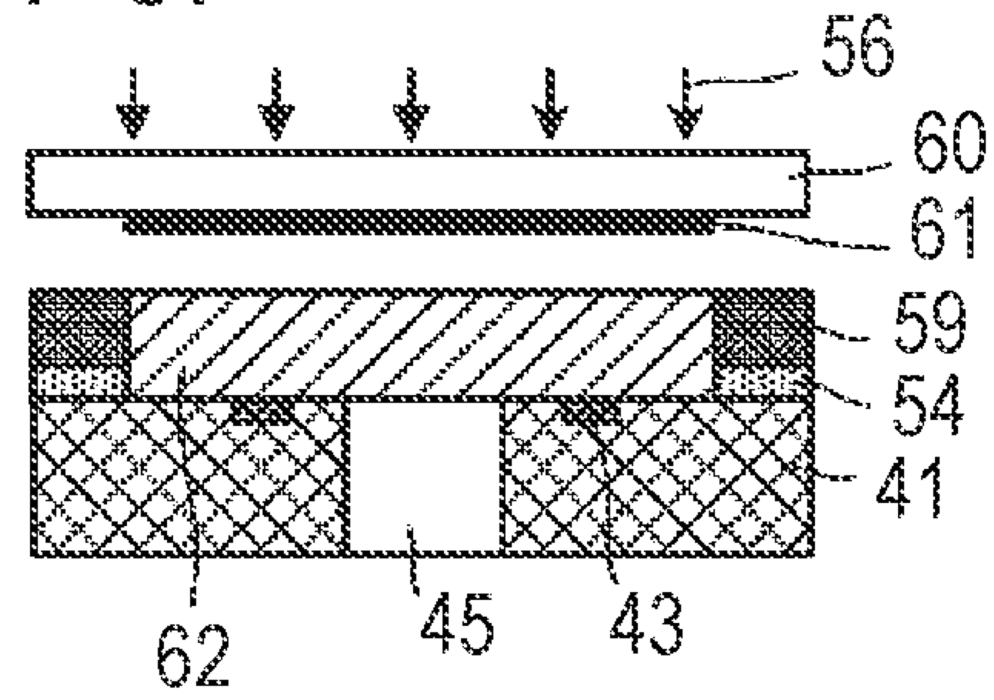


FIG. 5J

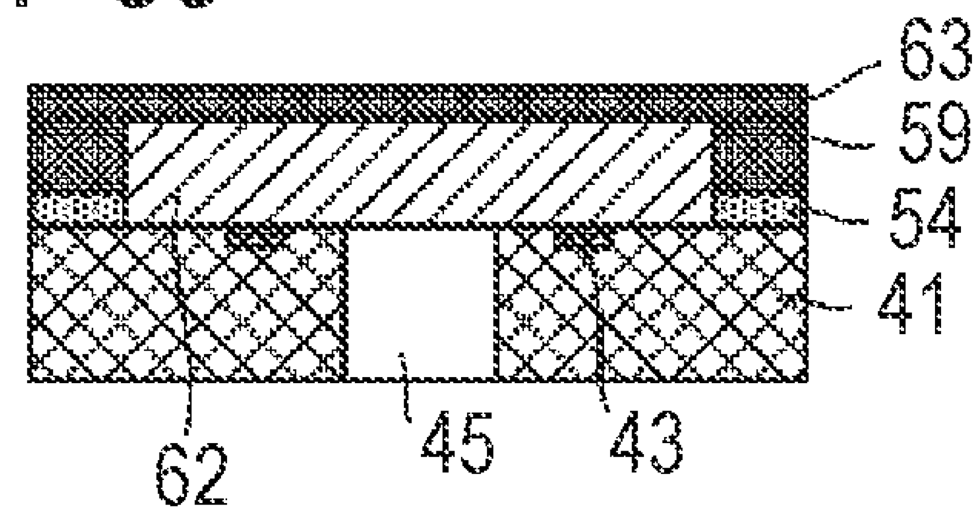


FIG. 5K

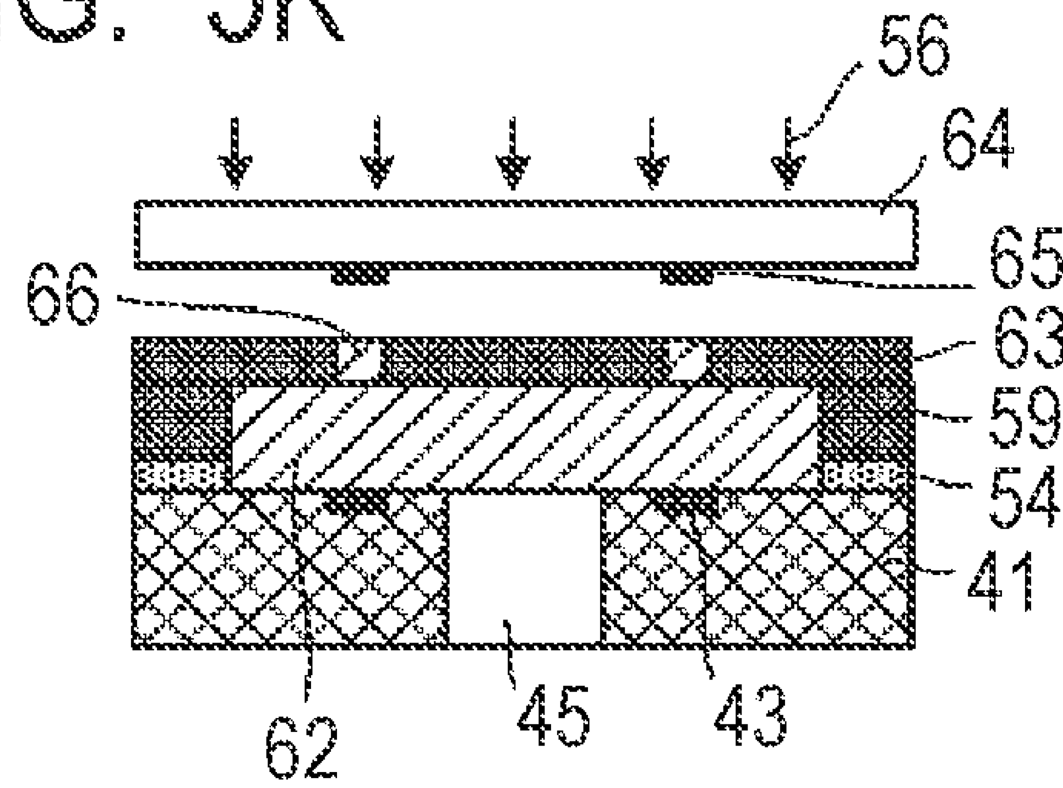


FIG. 5L

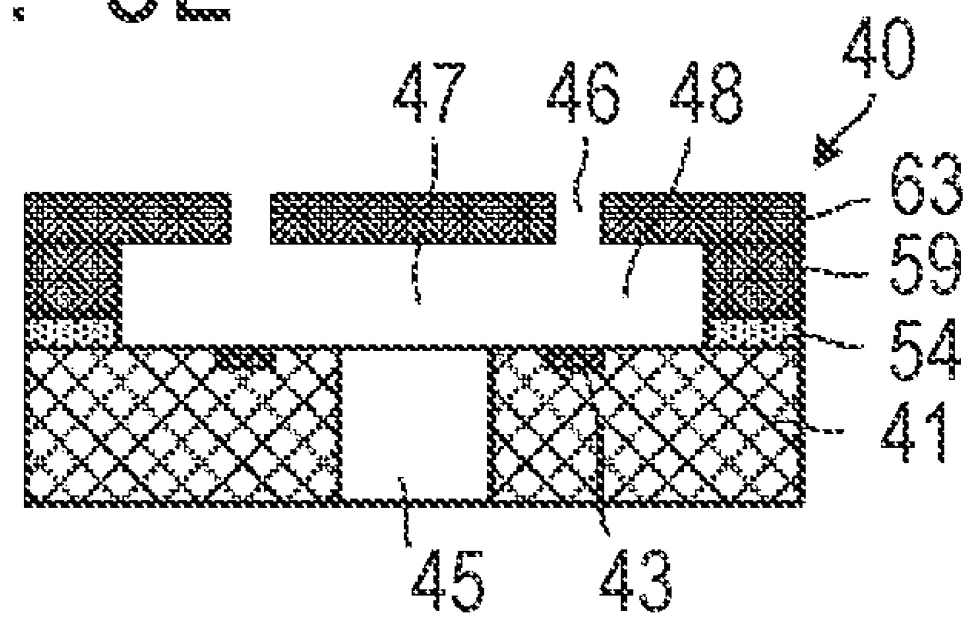


FIG. 6A

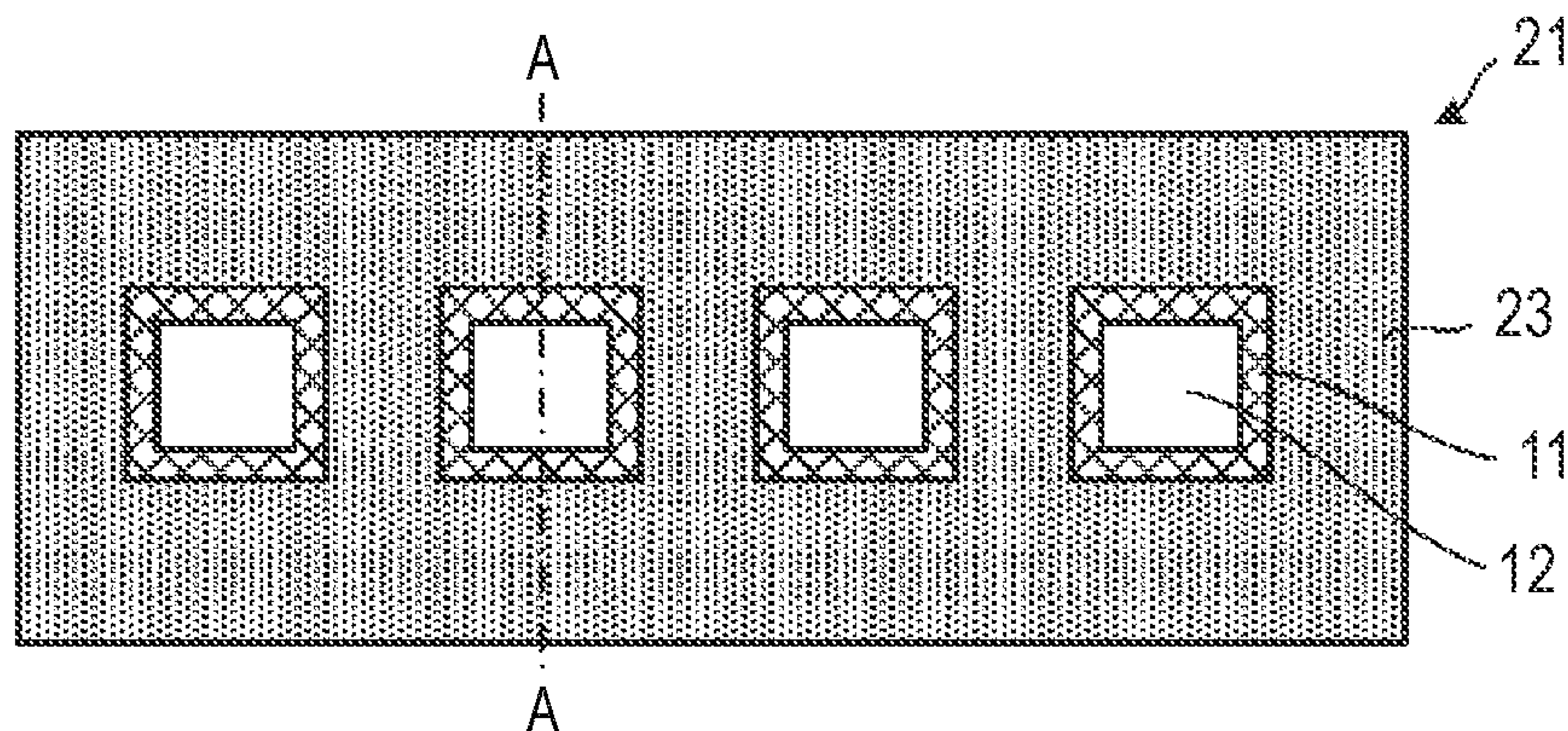


FIG. 6B

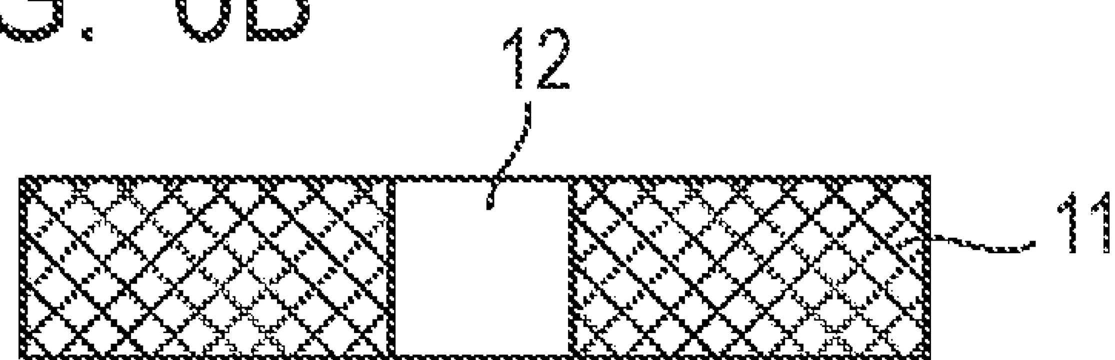


FIG. 6F

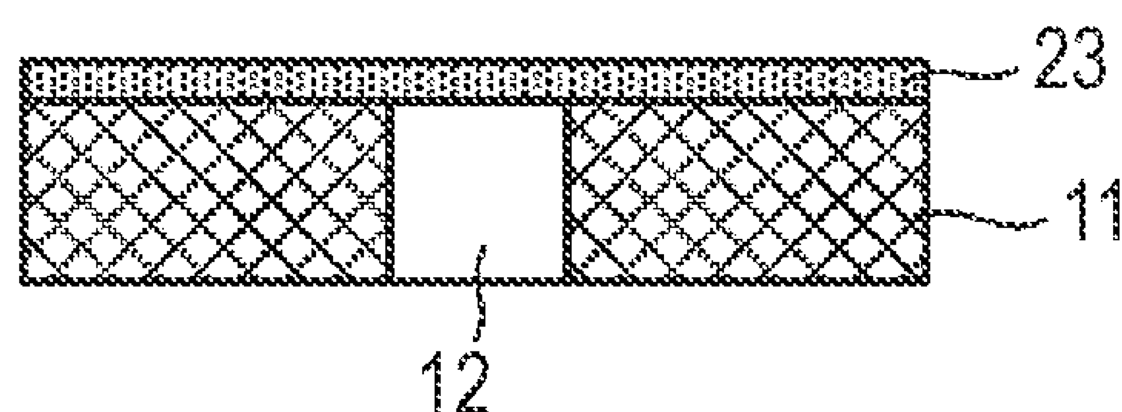


FIG. 6C

FIG. 6G

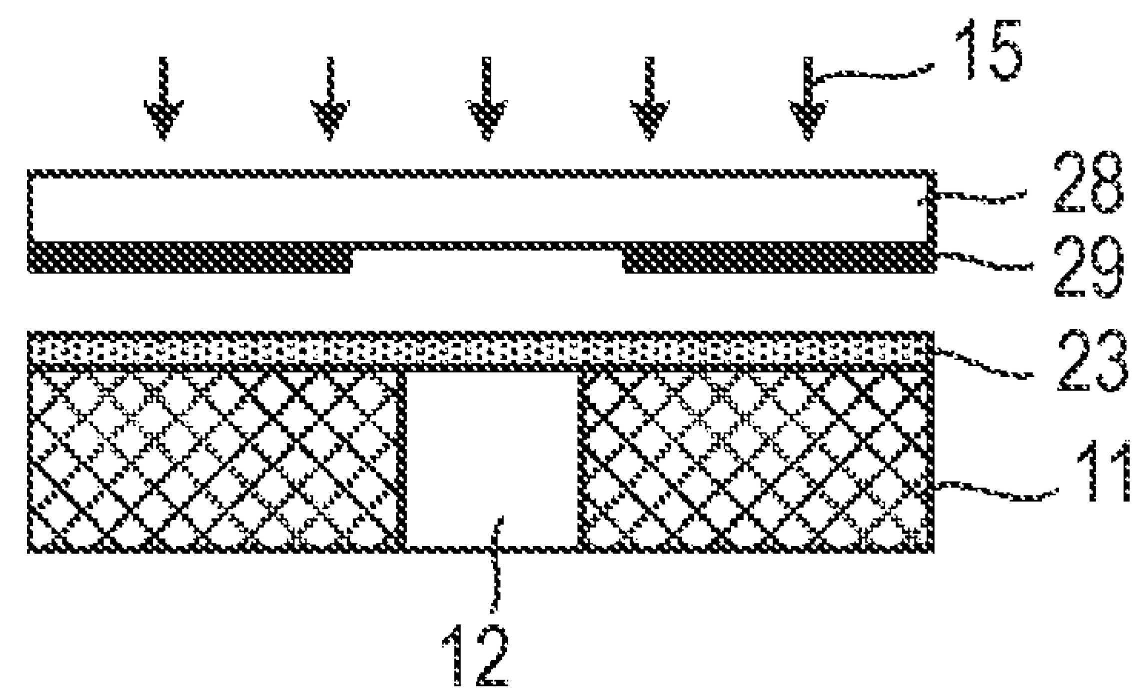


FIG. 6D

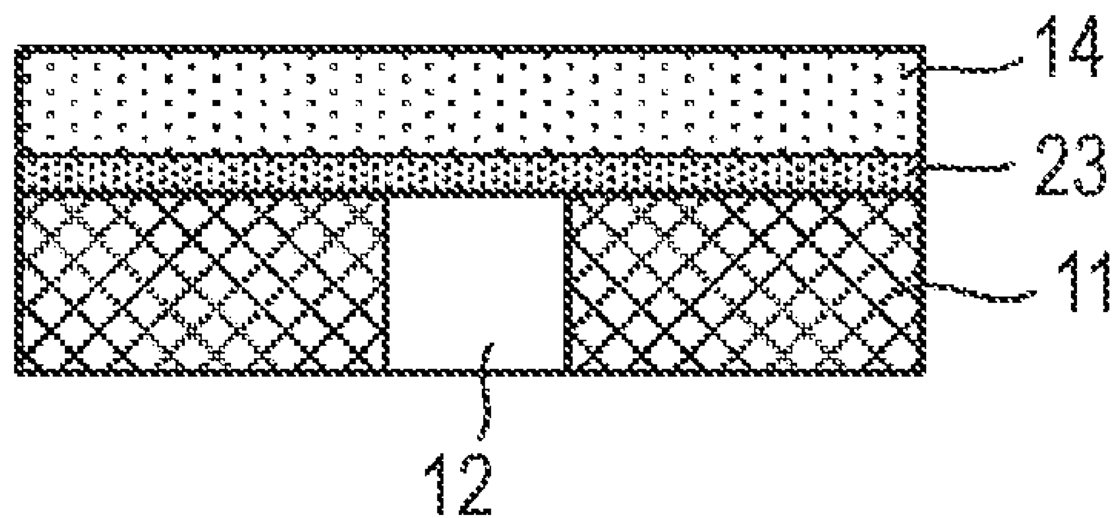


FIG. 6H

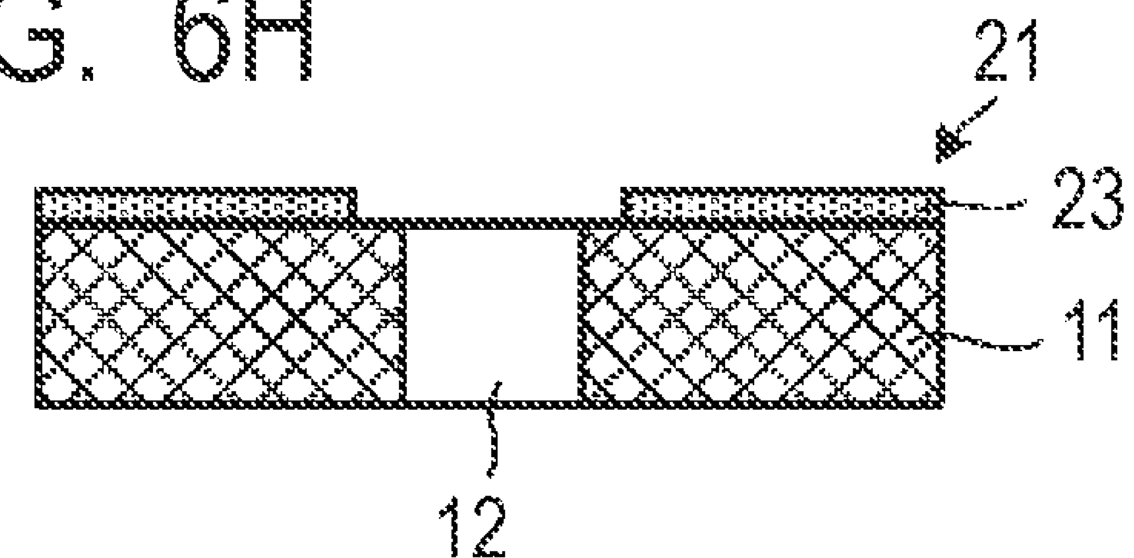


FIG. 6E

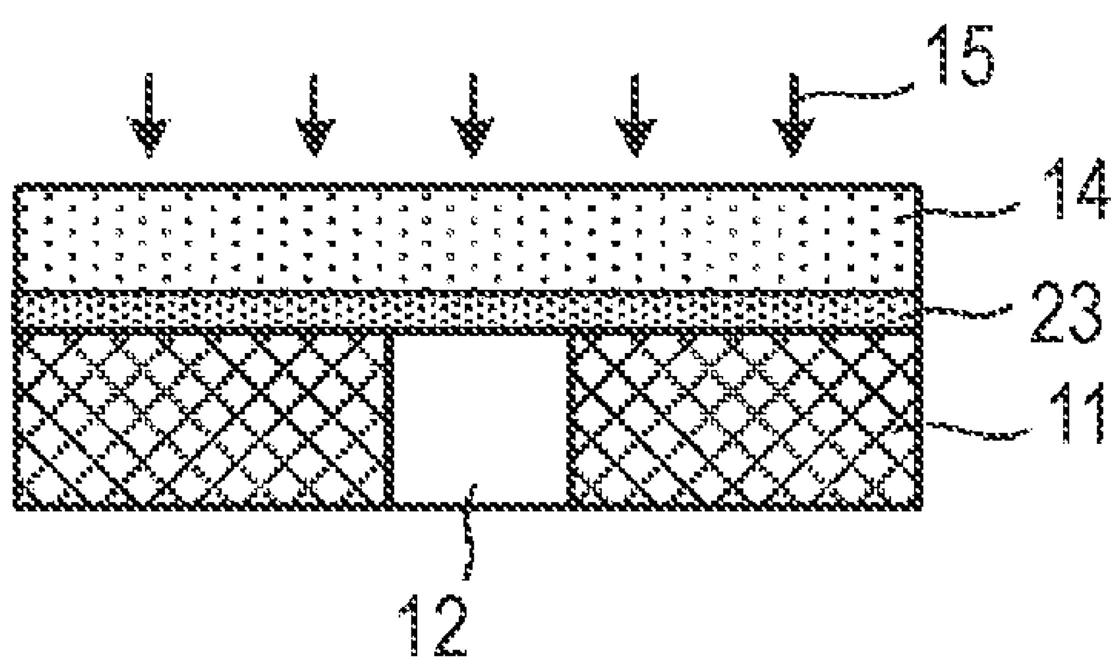


FIG. 7A

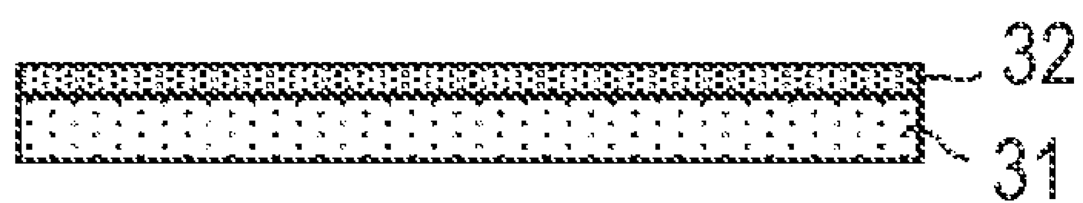
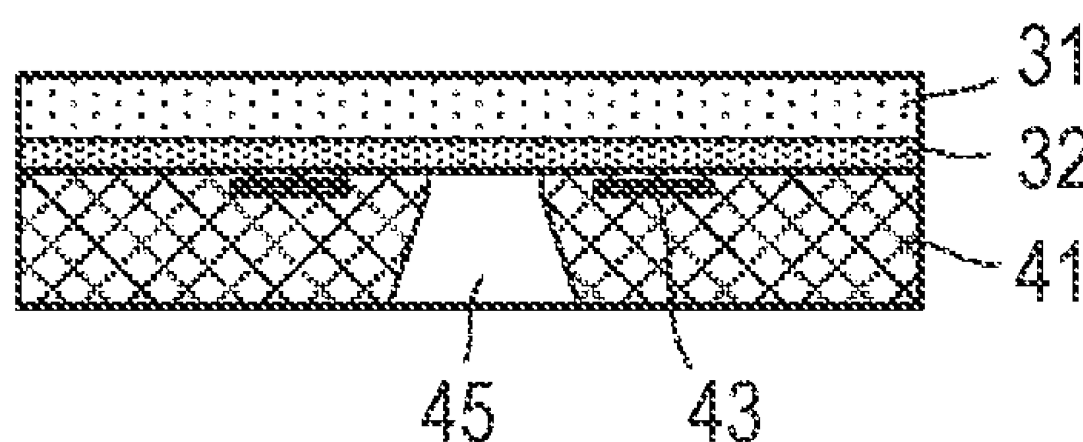


FIG. 7B



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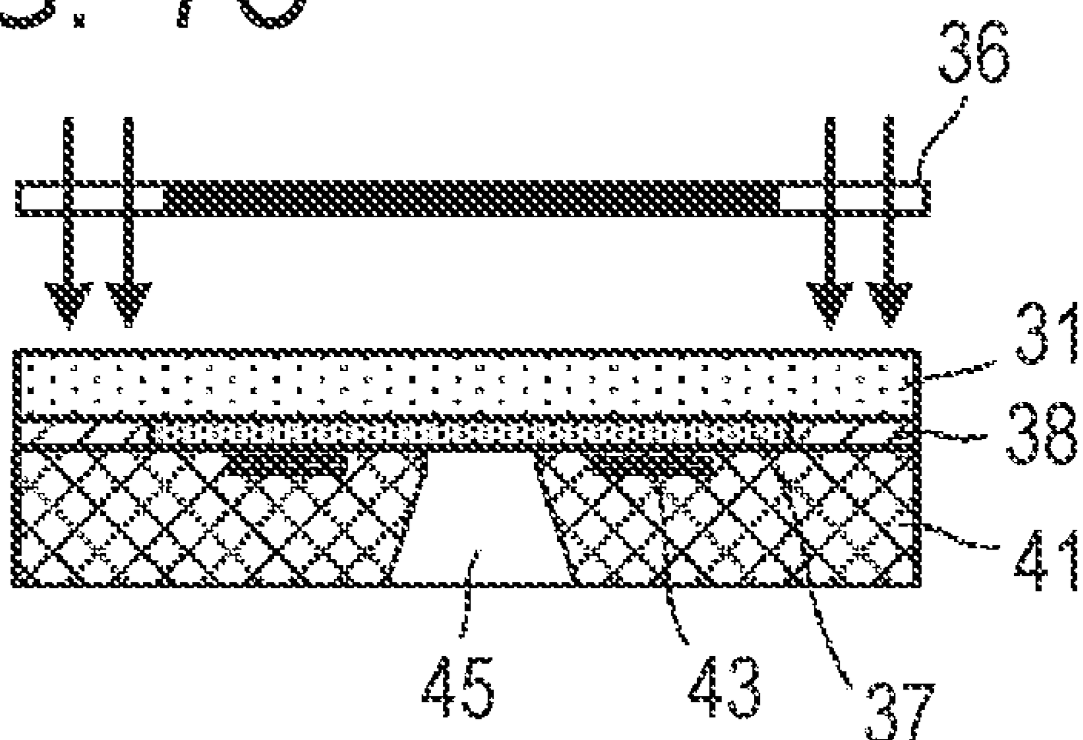

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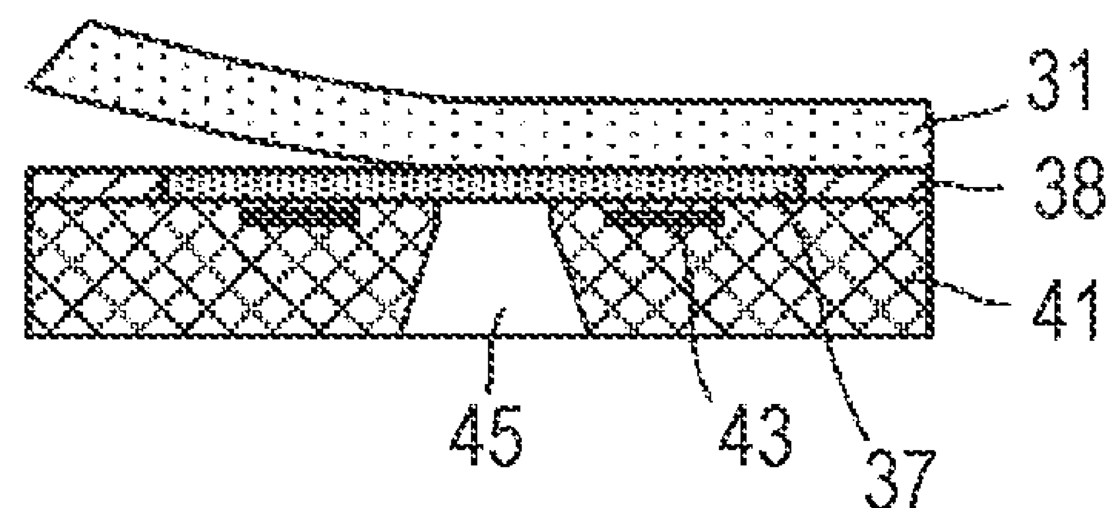
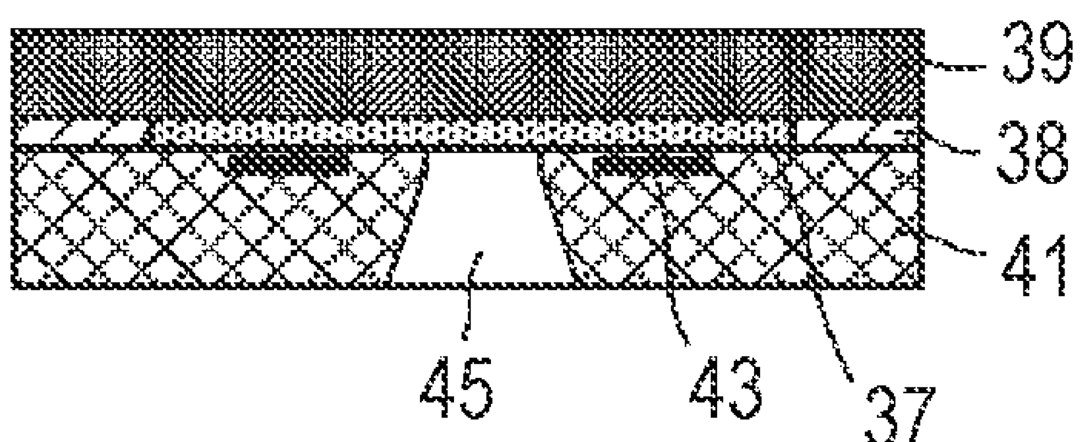


FIG. 7E



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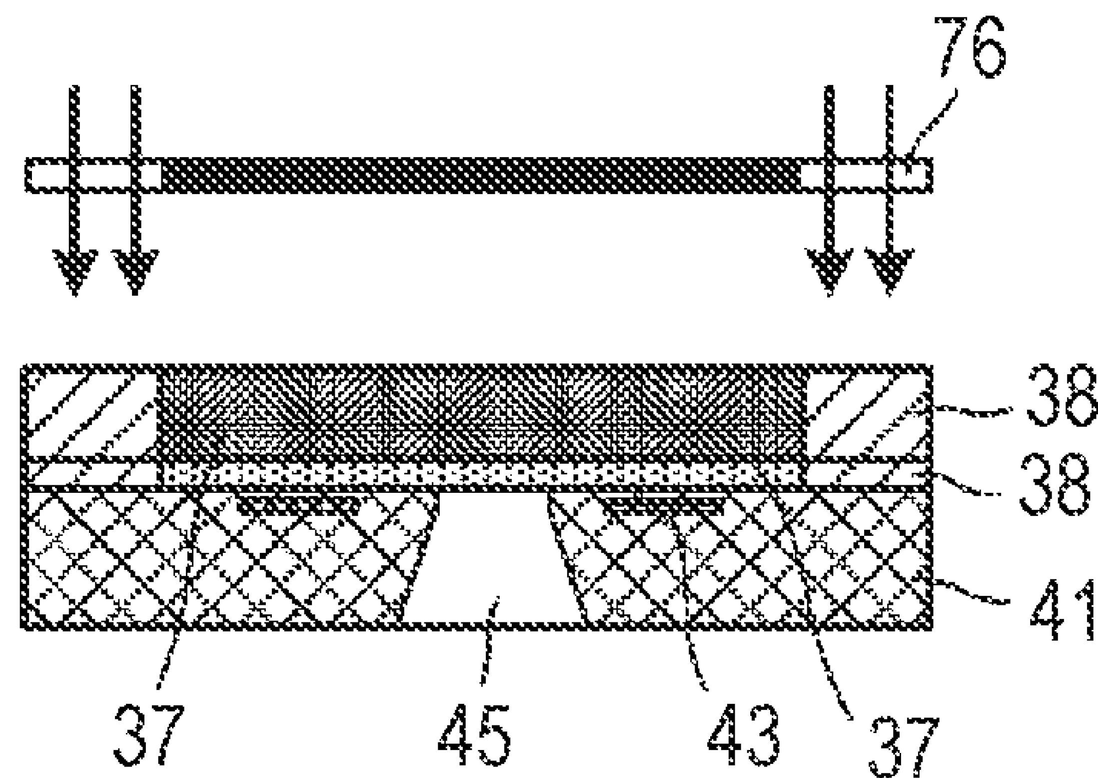


FIG. 7G

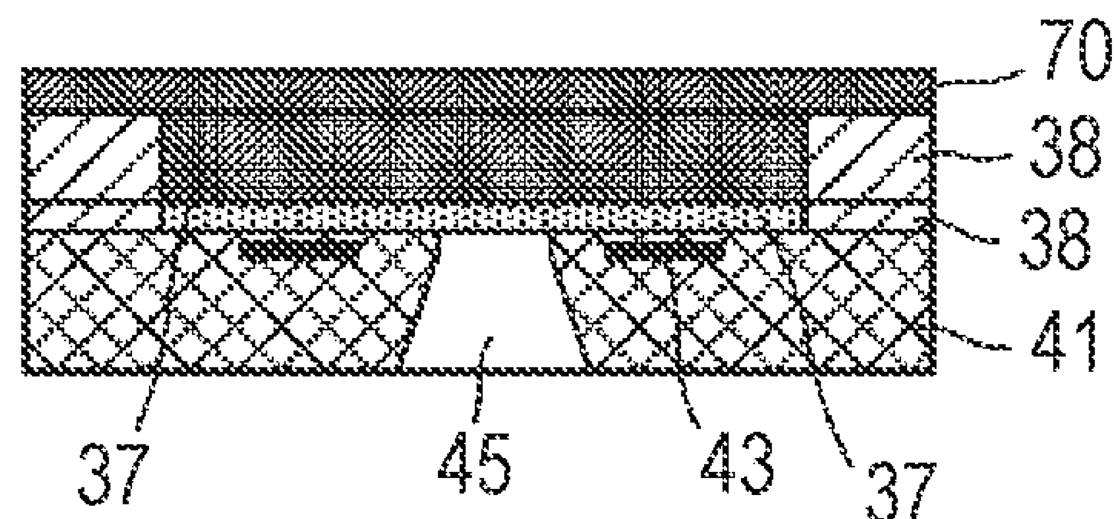


FIG. 7H

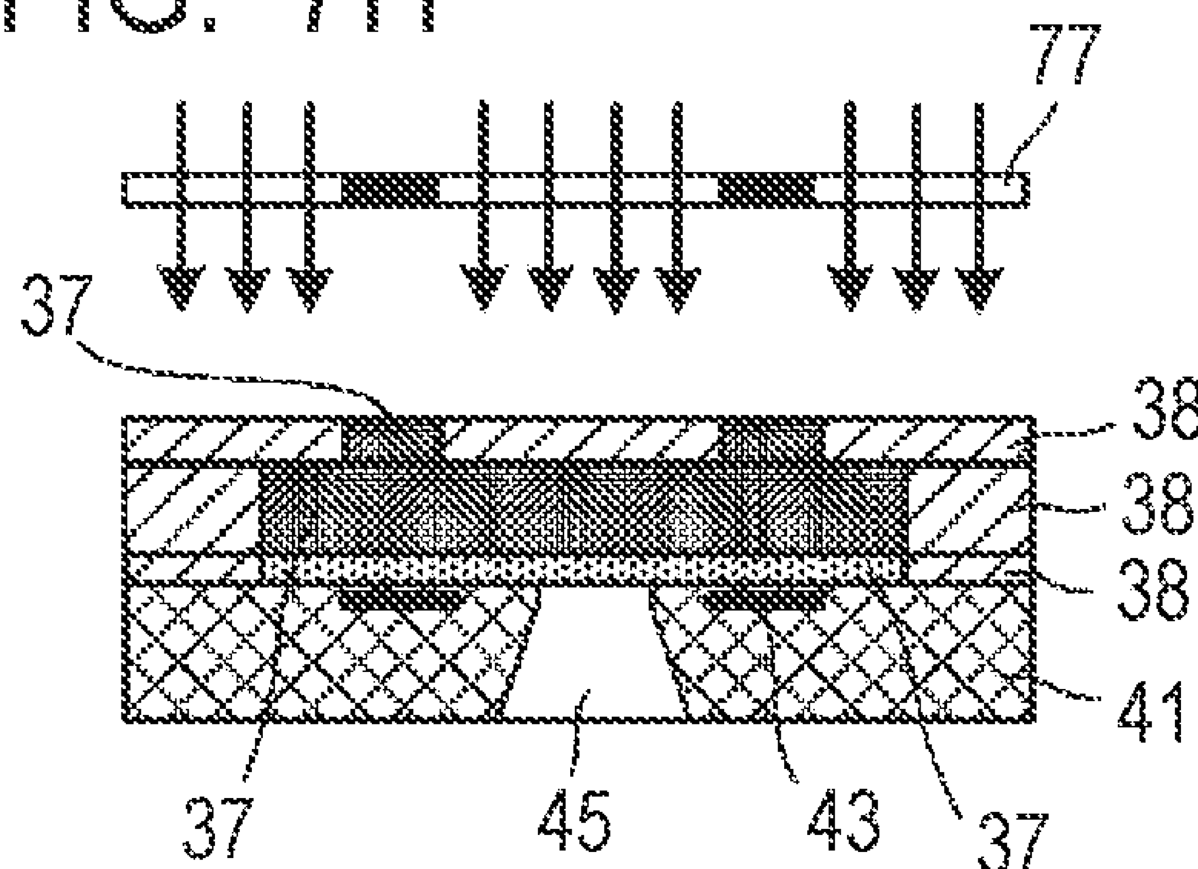


FIG. 7I

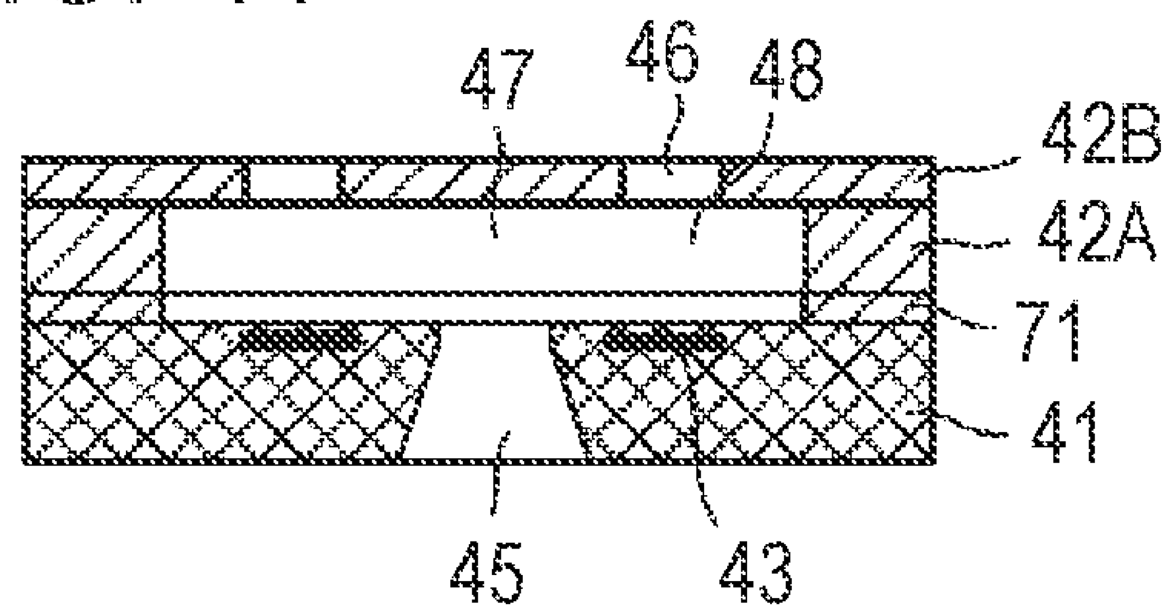


FIG. 8A

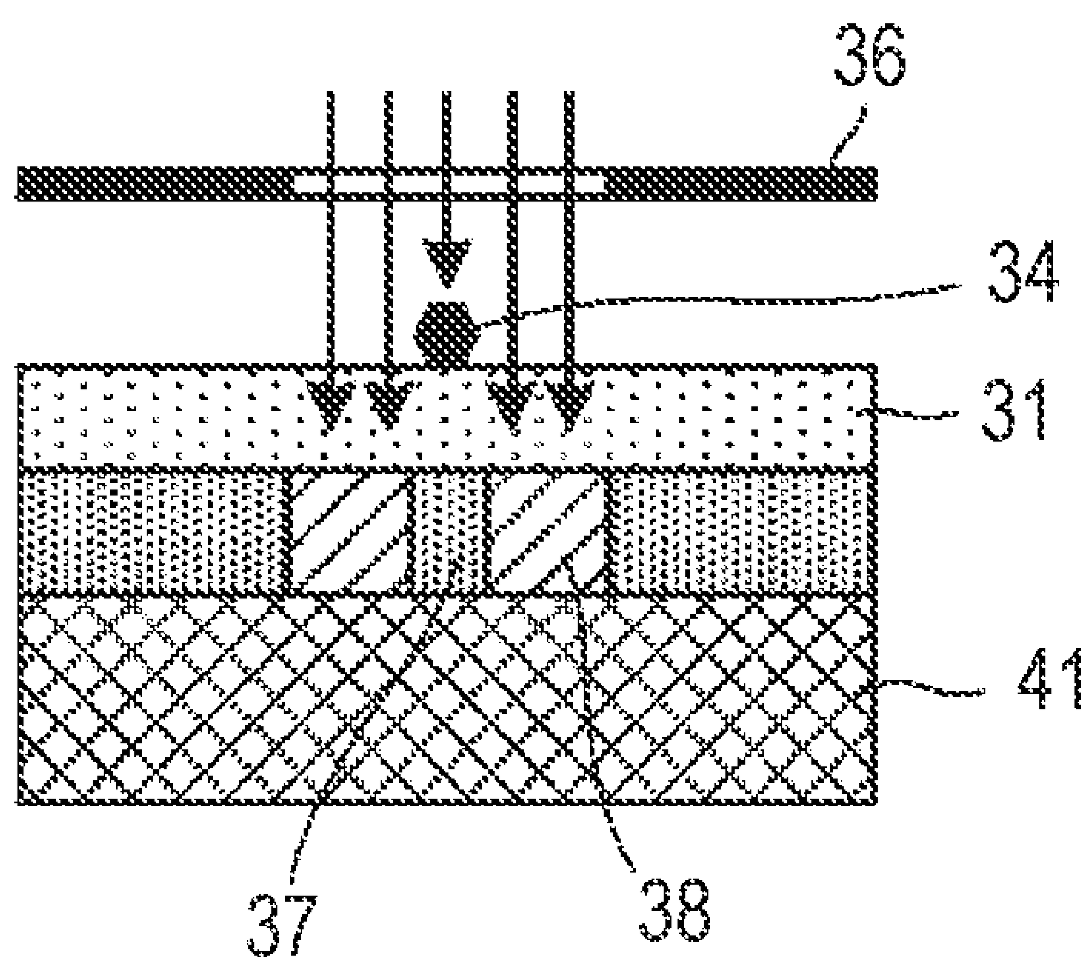


FIG. 8B

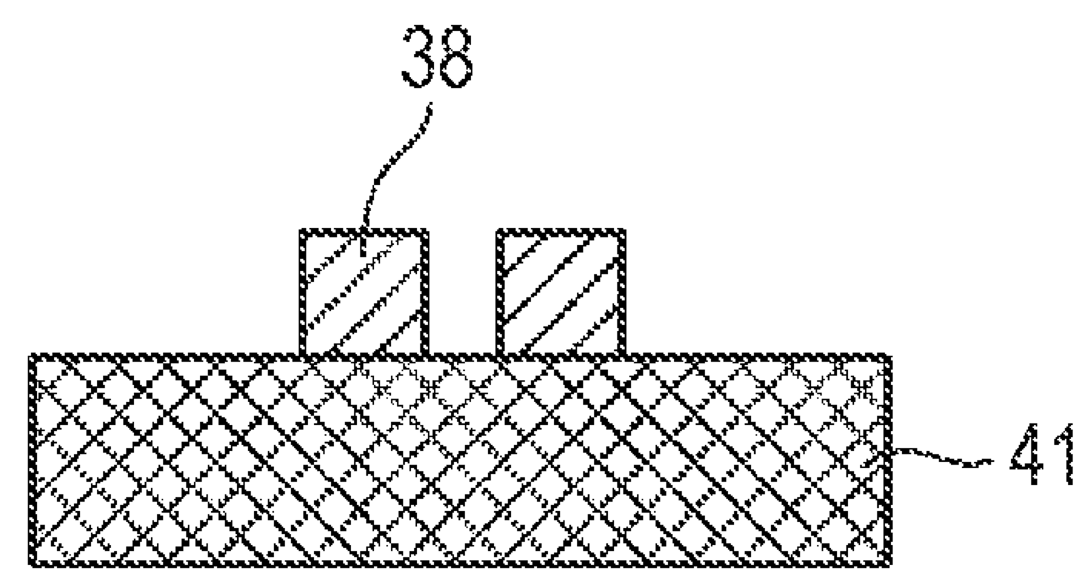


FIG. 9A

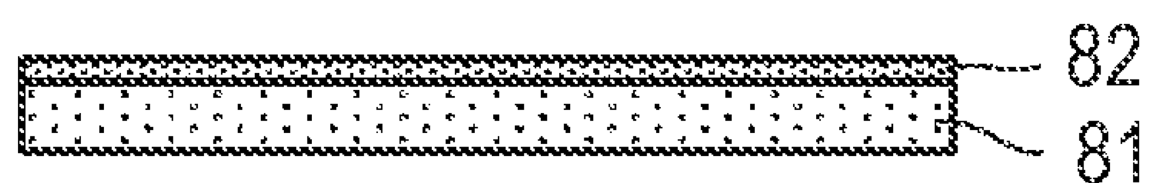


FIG. 9B

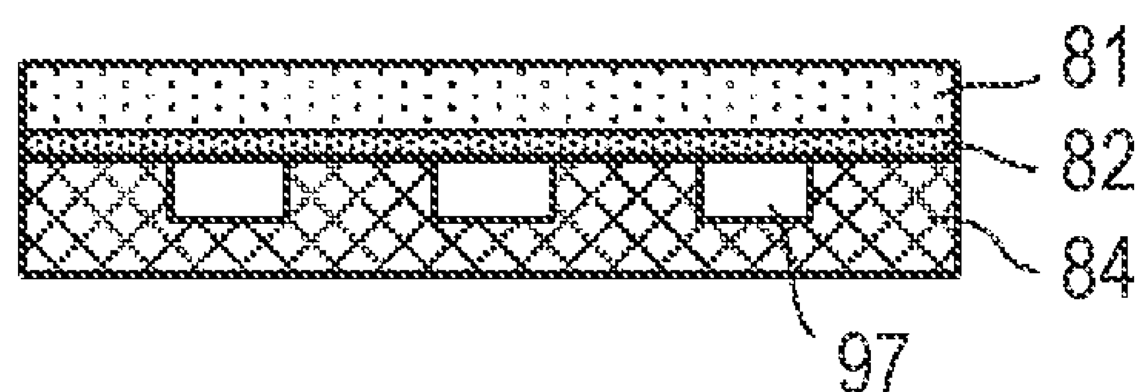


FIG. 9C

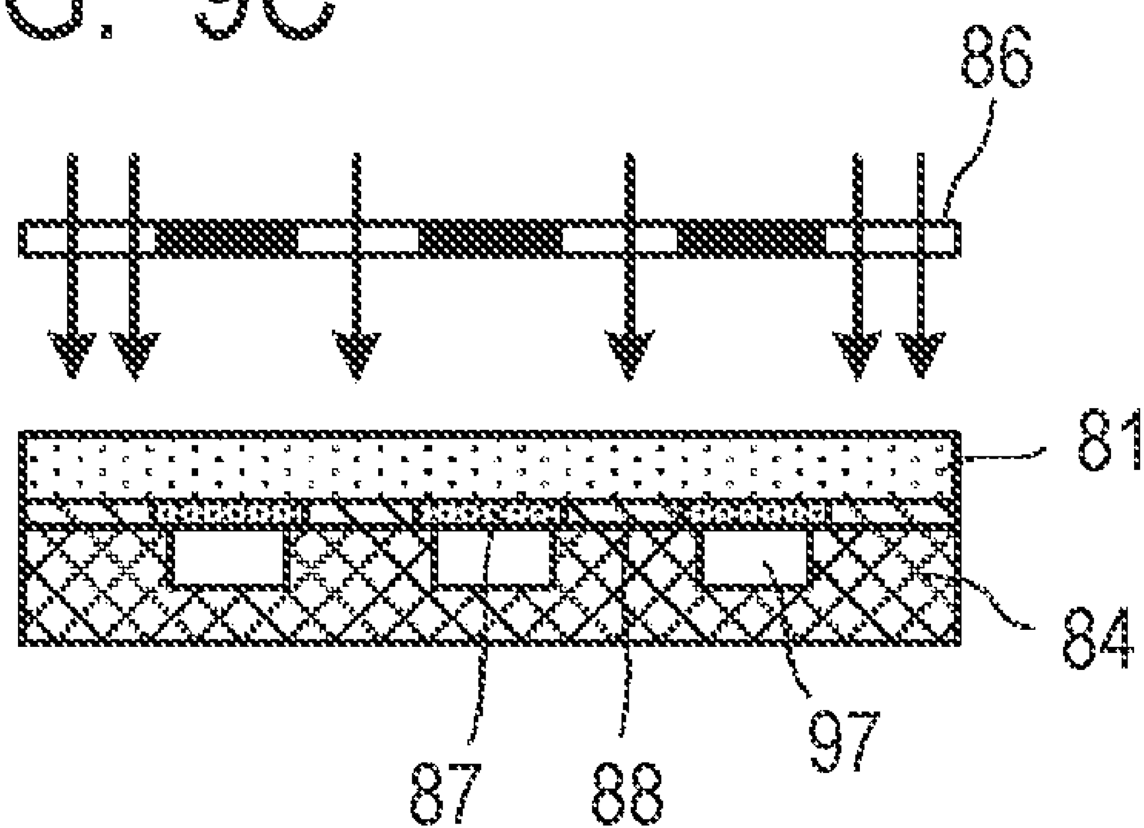


FIG. 9D

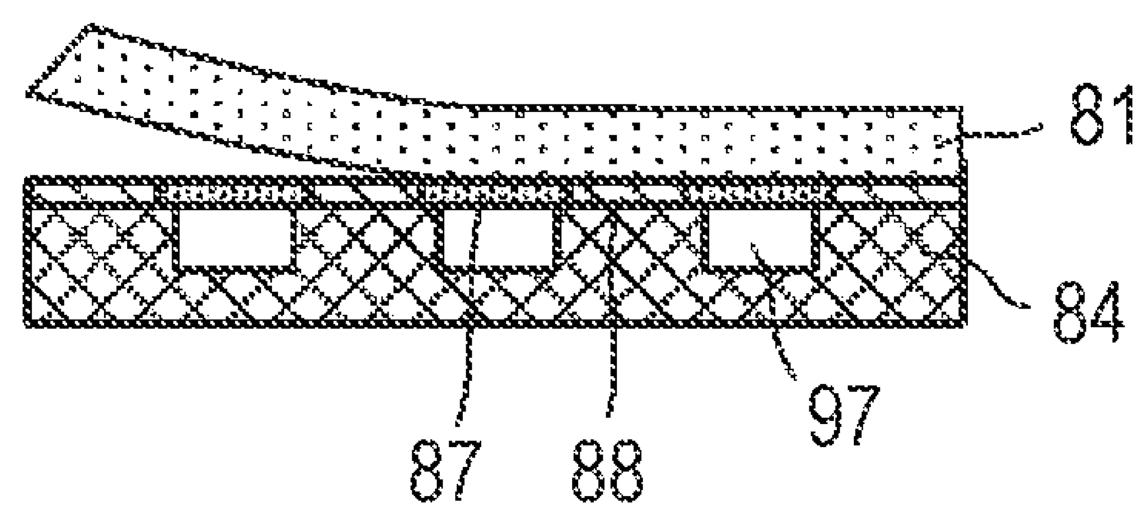


FIG. 9E

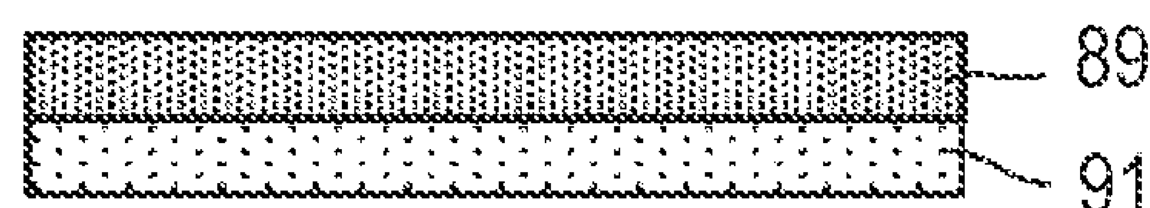


FIG. 9F

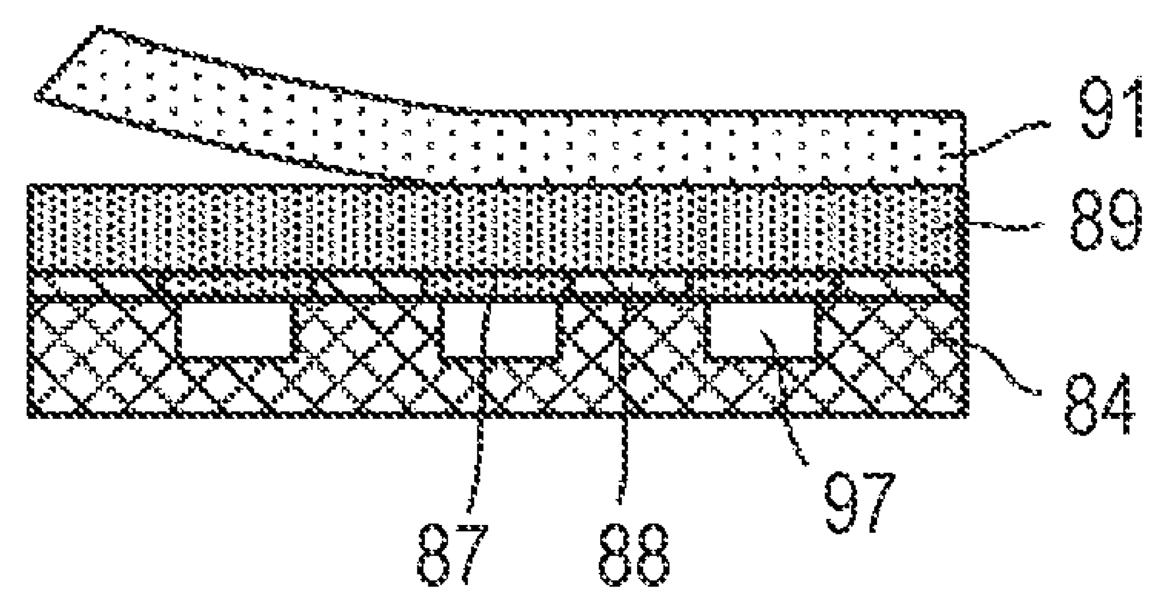


FIG. 9G

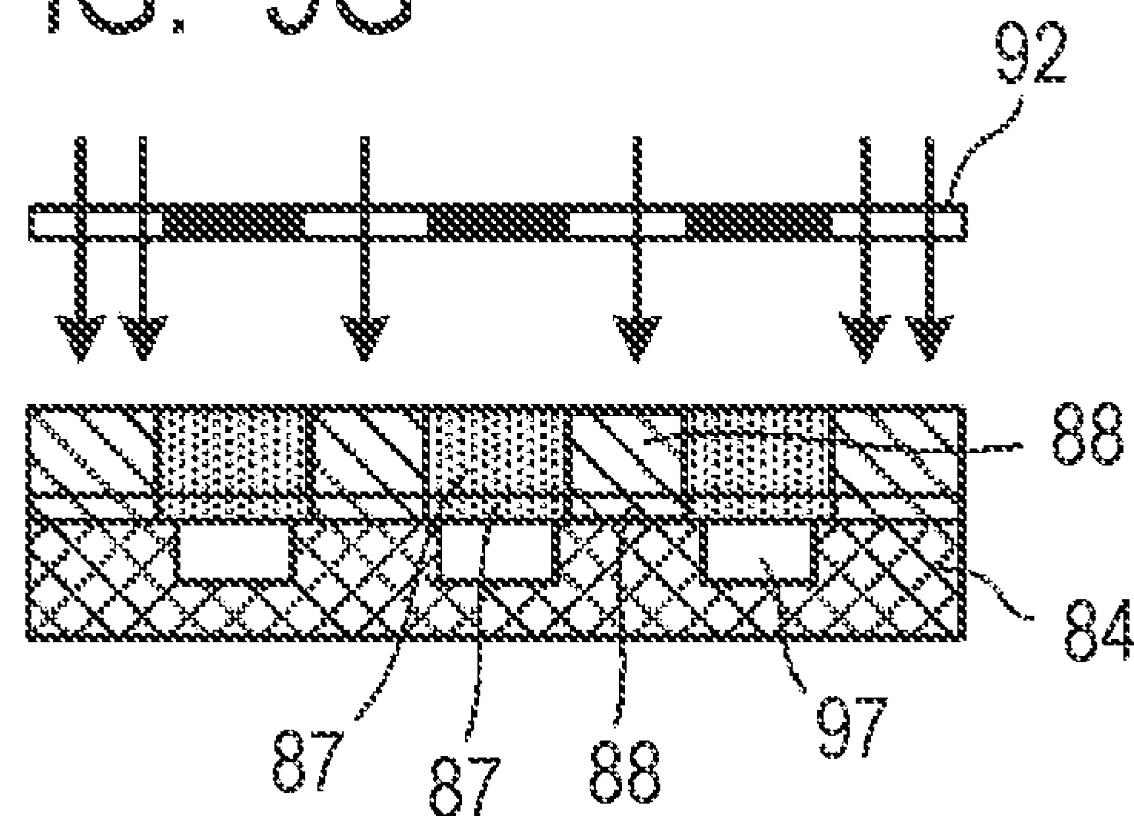
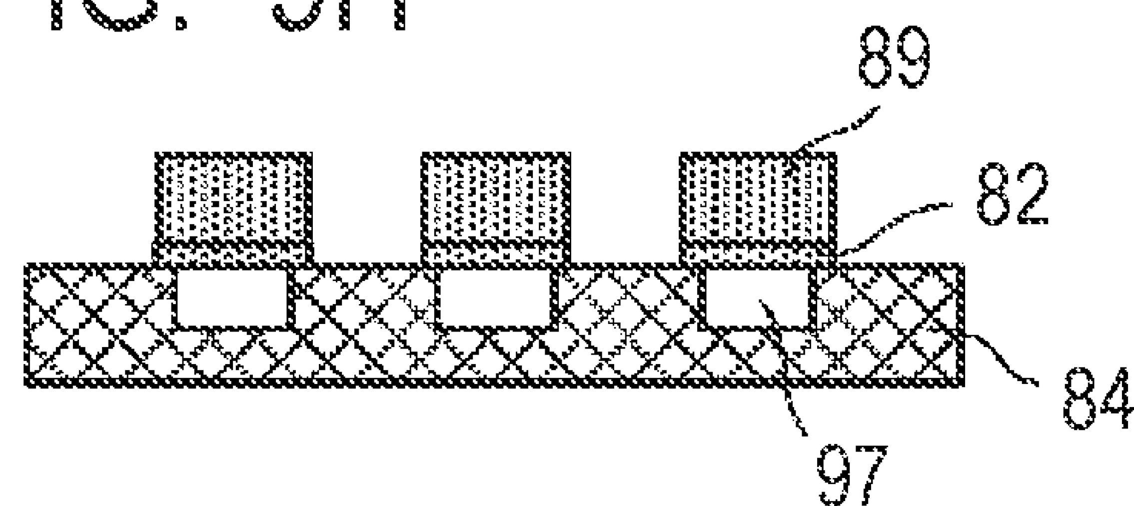


FIG. 9H



MANUFACTURING METHOD FOR STRUCTURE AND MANUFACTURING METHOD FOR LIQUID EJECTION HEAD

BACKGROUND OF THE INVENTION

Field of the Invention

The present disclosure relates to a manufacturing method for a structure for forming a structure having a photosensitive resin on a substrate and a manufacturing method for a liquid ejection head using the manufacturing method for the structure.

Description of the Related Art

A manufacturing method for forming a structure by using a substrate and a photosensitive layer made of a photosensitive resin such as a photoresist and a dry film is known. For example, the manufacturing method is used for manufacturing a liquid ejection head such as an ink jet recording head. In a manufacturing method for a structure, for example, a photosensitive layer may be formed on the support, the photosensitive layer may be laminated on a substrate and only the support may be peeled off to transfer the photosensitive layer onto the substrate. In a case where the photosensitive layer is thin and uncured, the photosensitive layer may be damaged when the support is peeled off. Japanese Patent Application Laid-Open No. 2017-202616 discloses a method in which a photoresist layer is formed on a base film which is a support, the substrate and the photoresist layer are laminated so as to be in contact with each other and the photoresist layer is subjected to pattern exposure via the support to be cured.

In the method described in Japanese Patent Application Laid-Open No. 2017-202616, since the pattern exposure of the photoresist layer is performed via the support, in a case where a foreign matter is present on the support, a pattern defect may occur.

SUMMARY OF THE INVENTION

A manufacturing method for a structure of the present disclosure includes preparing a first photosensitive layer on one surface of a first support; bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other; performing first exposure of the first photosensitive layer bonded to the substrate via the first support; removing the first support after the first exposure; performing second exposure of the first photosensitive layer after the first support is removed via a photomask; and developing the first photosensitive layer after the first exposure and the second exposure.

Further features of the present disclosure will become apparent from the following description of exemplary embodiments with reference to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a diagram illustrating a manufacturing method for a structure according to a first embodiment.

FIG. 1B is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1C is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1D is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1E is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1F is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1G is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1H is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1I is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1J is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1K is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 1L is a diagram illustrating a manufacturing method for the structure according to the first embodiment.

FIG. 2A is a diagram illustrating a manufacturing method for a structure according to a second embodiment.

FIG. 2B is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2C is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2D is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2E is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2F is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2G is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 2H is a diagram illustrating a manufacturing method for the structure according to the second embodiment.

FIG. 3 is a diagram illustrating a manufacturing method for a structure in a modification example according to the second embodiment.

FIG. 4 is a perspective view illustrating a liquid ejection head which is an example of a structure.

FIG. 5A is a diagram illustrating a manufacturing method for a liquid ejection head according to a third embodiment.

FIG. 5B is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5C is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5D is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5E is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5F is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5G is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5H is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. 5I is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. **5**J is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. **5**K is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. **5**L is a diagram illustrating a manufacturing method for the liquid ejection head according to the third embodiment.

FIG. **6**A is a diagram illustrating a manufacturing method for a structure according to a fourth embodiment.

FIG. **6**B is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**C is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**D is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**E is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**F is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**G is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **6**H is a diagram illustrating a manufacturing method for the structure according to the fourth embodiment.

FIG. **7**A is a diagram illustrating a manufacturing method for a liquid ejection head according to a fifth embodiment.

FIG. **7**B is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**C is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**D is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**E is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**F is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**G is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**H is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **7**I is a diagram illustrating a manufacturing method for the liquid ejection head according to the fifth embodiment.

FIG. **8**A is a diagram illustrating an influence of a foreign matter on the support.

FIG. **8**B is a diagram illustrating the influence of the foreign matter on the support.

FIG. **9**A is a diagram illustrating a manufacturing method for a structure according to a sixth embodiment.

FIG. **9**B is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**C is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**D is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**E is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**F is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**G is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

FIG. **9**H is a diagram illustrating a manufacturing method for the structure according to the sixth embodiment.

DESCRIPTION OF THE EMBODIMENTS

An aspect of the present disclosure is to provide a manufacturing method for a structure having a step of exposing a photosensitive layer via a support and capable of suppressing occurrence of a pattern defect and a manufacturing method of a liquid ejection head to which this manufacturing method is applied.

Next, an exemplary embodiment of the present disclosure will be described with reference to the drawings. Each embodiment described below is subject to various technically exemplary limitations. However, the present invention is not limited to the embodiments, manufacturing examples and other specific methods described in the present specification as long as these conform to the technical idea of the present disclosure. In the following description, the same reference numerals are given to the configurations having the same function in the drawings and the description of the overlapping portion may be omitted.

First Embodiment

FIGS. **1**A to **1**H are diagrams illustrating a manufacturing method for a structure according to a first embodiment and FIG. **1**A is a plan view of a structure **10**. FIGS. **1**B to **1**H are cross-sectional views taken along line A-A of FIG. **1**A and illustrate a manufacturing process in the present embodiment step by step. In particular, FIG. **1**H illustrates a cross section of the finally formed structure **10**. FIGS. **1**I to **1**L illustrate a manufacturing process step by step in a case where a foreign matter **18** is present on a support **14** described later. In the present embodiment, a pattern made of a photosensitive resin is formed on one surface of a substrate **11** on which an opening **12** is formed to form the structure **10**. In the structure **10**, as illustrated in FIGS. **1**A and **1**H, the photosensitive resin is patterned so as to surround the opening **12** at a position where the opening **12** is provided on the substrate **11** and to form an opening **20** larger than the opening **12**. At the opening **20**, the surface of the substrate **11** is exposed. The opening **12** is formed as, for example, a through-hole penetrating the substrate **11**.

FIG. **1**B illustrates a cross section of the substrate **11**. For example, the substrate **11** can be made of one of single crystal silicon, glass and ceramic. A planar shape of the opening **12** may be, for example, one of a circle and a quadrangle. In the drawing, the planar shape of the opening **12** is substantially square. The angle formed by a side wall of the opening **12** and the surface of the substrate **11** may be vertical and the opening **12** may have a tapered cross-sectional shape. A protective film (not illustrated) may be formed on one of both surfaces of the substrate **11** and on the side wall of the opening **12**. The present invention is not limited to the shape of the opening **12** formed in the substrate **11**.

As illustrated in FIG. **1**C, a dry film **13** formed on the support **14** which is a first support is prepared separately from the substrate **11**. The dry film **13** is a first photosensitive layer supported by one surface of the support **14** and having photosensitivity and is normally made of a photosensitive resin. As an example, the dry film **13** is made of, for example, a negative photosensitive resin. The dry film **13** as a negative photosensitive resin is desirably made of a

negative photosensitive resin composition containing, for example, one of an epoxy resin, an acrylic resin and a urethane resin. As the epoxy resin, for example, one of bisphenol A type, cresol novolac type and alicyclic epoxy resin can be used and as the acrylic resin, for example, polymethyl methacrylate can be used. Examples of the urethane resin include various types of polyurethane. As the solvent used for the negative photosensitive resin, for example, one or more solvents selected from the group consisting of propylene glycol methyl ether acetate (PGMEA), diglyme, cyclohexane, methyl ethyl ketone and xylene can be used. Additives may be appropriately added to this solvent, if necessary. The dry film **13** is formed on the support **14** by dissolving a negative photosensitive resin in a solvent and applying the mixture to the support **14** and removing the solvent. As a negative photosensitive resin composition, for example, one of commercially available "SU-8 series" and "KMPR (registered trademark)-1000" manufactured by Nippon Kayaku Co., Ltd. and "TMMR (registered trademark) 52000" and "TMMF (registered trademark) 52000" manufactured by Tokyo Ohka Kogyo Co., Ltd. can also be used. It is also possible to use a positive photosensitive resin as described later. As the positive photosensitive resin, for example, a commercially available photosensitive resin composition such as "PMER (registered trademark)" manufactured by Tokyo Ohka Kogyo Co., Ltd. can be used. The dry film **13** on the support **14** may be formed by, for example, one of a spin coating method, a slit coating method and a spray coating method and may be subjected to the baking treatment. In the spin coating method, a thin film of the coating liquid is formed by using centrifugal force by rotating the table on which the support **14** on which the coating liquid is dropped is placed at high speed. In the slit coating method, a thin film is formed directly on a portion of the support **14** on which the thin film is formed. In the spray coating method, a thin film of the coating liquid is formed by spraying the atomized coating liquid on the support **14**.

As the support **14**, for example, a support made of one of a film, a glass substrate and a silicon substrate is used and in consideration of the ease of peeling off the support **14** after the dry film **13** is transferred to the substrate **11**, the film can be used. Here, the reason why the dry film **13** is formed on the support **14** is that in the present embodiment, the thickness of the dry film **13** is, for example, several μm or less and it is difficult to laminate the dry film **13** alone on the surface of the substrate **11** on which the openings **12** are formed. On the other hand, since it is difficult to develop the dry film **13** with the support **14** laminated, it is necessary to remove the support **14** before a developing step. In addition, from the viewpoint of exposing the dry film **13** via the support **14**, as the support **14**, an optical film can be used which is unlikely to be diffusely reflected, has a high transmittance and further has a coefficient of thermal expansion of approximately 10^{-4} cm/cm ° C. or less. As long as it satisfies such characteristics, a normal film such as polypropylene (PP), polycarbonate (PC), polyethylene terephthalate (PET) and polyimide (PI) can be used as the support **14**. More desirably, as the support **14**, a film formed of a cycloolefin polymer and a cycloolefin copolymer is used. As the cycloolefin polymer film and the cycloolefin copolymer film, ZEONOA film (registered trademark) ZF**14** and ZEONOA film (registered trademark) ZF**16** (manufactured by Zeon Corporation), F**1**-film (manufactured by GUNZE LIMITED), G**3**-film (manufactured by Dexerials Corporation) and Apel (registered trademark) (manufactured by Mitsui Chemicals, Inc.) can be used. The thickness of the support **14** is desirably in the range of, for example, 30 to 150 μm and more desirably in the range of 50 to 100 μm. In order to facilitate peeling, a support **14** whose surface is subjected to a mold release treatment may be used. When the exposure wavelength used in a first and second exposing steps described later is an ultraviolet wavelength, the support **14** can have a light transmittance of 70% or more in the wavelength region of 248 to 436 nm.

In a case where a reduction optical system is used for exposure via the support **14**, since the focus position shifts depending on the thickness and the refractive index of the support **14**, it is necessary to compensate for the focus position. Here, with respect to the moving direction of the focus position, moving the focus from the support **14** to the substrate **11** is expressed as negative (minus). For example, when PET (refractive index 1.6) having a thickness of 100 μm is used for the support **14**, the surface of the support **14** may be set to 0 μm and the focus position may be shifted to the side of the substrate **11** by approximately—65 μm. Similarly, when a cycloolefin polymer (refractive index 1.53) having a thickness of 50 μm is used for the support **14**, the focus position may be shifted to the side of the substrate **11** by approximately—33 μm.

Next, as illustrated in FIG. **1**D, the dry film **13** is attached to the substrate **11** via the support **14** so that the dry film **13** is in contact with one surface of the substrate **11** to bond the substrate **11** and the dry film **13**. The dry film **13** is transferred to and laminated on the substrate **11** via the support **14** by, for example, a laminating method while applying temperature and pressure, for example. In the implementation of the laminating method, for example, a roll-type transfer under vacuum can be performed in consideration of the discharge property of bubbles so that bubbles do not enter between the substrate **11** and the dry film **13**. In order to improve the adhesion between the substrate **11** and the dry film **13**, for example, a silane material treatment may be performed on the surface of the substrate **11** in advance.

Next, as illustrated in FIG. **1**E, a first exposing step of exposing the dry film **13** via the support **14** is performed. The type of light **15** used for exposure is not particularly limited as long as the light can expose the dry film **13** to light and transmits the support **14** and ultraviolet rays can be used. The dry film **13** is divided into a first region, which is a region where the substrate **11** is exposed at the opening **12** and around the opening **12** (that is, region corresponding to the opening **20**) by the developing step, which is a subsequent step and a second region, which is a region left on the substrate **11** in the developing step. In the first exposing step, it is necessary to irradiate with the light **15** with an exposure amount that can cure the dry film **13** in order to improve the adhesion to the substrate **11** and the first region of the dry film **13** is a portion finally removed in the developing step. Therefore, the first exposing step can be performed with an exposure amount less than the resolution limit minimum exposure amount E_{th} of the dry film **13**. The resolution limit minimum exposure amount is the minimum exposure amount for forming a residual film of the photosensitive resin after exposure at the resolution limit of the photosensitive resin with respect to the negative photosensitive resin. In the following description, the resolution limit minimum exposure amount is also simply referred to as the minimum exposure amount. As illustrated in FIG. **1**E, the first exposing step may be full exposure without setting a light-shielding region by a photomask. When the exposure amount at this time is an exposure amount that can cure the dry film **13** and is less than the minimum exposure amount

E_{th}, it is possible to remove the first region in the developing step while preventing the dry film **13** from peeling off from the substrate **11** when the support **14** is removed in the next step.

Next, as illustrated in FIG. **1**F, the support **14** is removed from the substrate **11** by peeling the support **14** from the dry film **13**. Since the dry film **13** is cured by the first exposing step and the film strength and adhesion to the substrate **11** are improved, it is possible to prevent the dry film **13** from peeling from the substrate **11** when the support **14** is removed. Here, it is more desirable that the dry film **13** is tented on the opening **12** after the support **14** is removed. However, since the first region is a region removed in a later developing step, the dry film **13** at the position of the opening **12** may remain on the side of the support **14**. Before removing the support **14**, the dry film **13** may be heat-treated using, for example, a hot plate.

Next, as illustrated in FIG. **1**G, a second exposing step is performed. In the second exposing step, pattern exposure is performed by shielding the first region of the dry film **13** with a light-shielding portion **17** of a photomask **16** and irradiating with light **15**. In a case where a photomask is used in the first exposing step, the distance between an end portion of the light-shielding portion in the first exposing step and an end portion of the light-shielding portion **16** in the second exposing step is required to be larger than the amount of deviation in alignment between these exposing steps. Specifically, the distance between the end portion of the light-shielding portion in the first exposing step and the end portion of the light-shielding portion **16** in the second exposing step is desirably, for example, 1 μm or more and more desirably 0.5 μm or more. The exposure amount in the second exposing step can be an exposure amount equal to or more than the minimum exposure amount of the dry film **13** so that the second region not shielded by the light-shielding portion **17** is left even after the developing step.

Next, the developing step is performed to remove the first region of the dry film **13**. As a result, as illustrated in FIG. **1**H, the structure **10** having the second region of the dry film **13** is formed on the substrate **11**. As a developing solution, for example, one of PGMEA, tetrahydrofuran, cyclohexanone, methyl ethyl ketone and xylene can be used. In a case where the dry film **13** is made of a chemically amplified photosensitive resin composition, the dry film **13** may be heat-treated using a hot plate before the development of the dry film **13**. In addition, the dry film **13** may be cured by performing a heat treatment after the developing step.

Next, the formation of the structure **10** in a case where the foreign matter **18** is present on the support **14** in the first exposing step will be described with reference to FIGS. **1**I to **1**L. Examples of the foreign matter **18** include those contained in the support **14** itself, those attached to the support **14** and step particles (fine particles). Examples of the material of the foreign matter **18** include metal, silicon, inorganic material, resin and fiber waste. As illustrated in FIG. **1**I, when the foreign matter **18** that does not transmit the light **15** used for exposure is present on the support **14**, an unexposed portion **19** may be formed when the dry film **13** is exposed via the support **14**. Therefore, in the manufacturing method for the structure in the related art, the unexposed portion **19** may cause a pattern defect after development. Specifically, in a case where the negative dry film **13** is used, the unexposed portion **19** shielded by the foreign matter **18** is removed by development, which causes a recess (hole)—shaped pattern defect. In a case where the dry film **13** is of the positive, the unexposed portion **19** shielded by the foreign matter **18** causes a pattern defect that is a development residue.

Also in the present embodiment, in a case where the foreign matter **18** is present on the surface of the support **14**, as illustrated in FIG. **1**J, the unexposed portion **19** due to the foreign matter **18** is present in the second region of the dry film **13** after a first exposing step is performed at the stage where the support **14** is removed. Thereafter, as illustrated in FIG. **1**K, a second exposing step is performed. At this time, by setting the exposure amount so that the second region can be left in the developing step, that is, the exposure amount equal to or more than the minimum exposure amount of the dry film **13**, the unexposed portion **19** existing in the second region is eliminated. When the developing step is performed, the first region is removed and as illustrated in FIG. **1**L, the structure **10** having the second region of the dry film **13** is formed on the substrate **11**. In this structure **10**, the pattern defect caused by the foreign matter **18** is suppressed.

According to the present embodiment, the first exposing step of exposing the dry film **13** via the support **14** which is the first support, a step of removing the support **14** and the second exposing step of exposing the dry film **13** without the support **14** are performed. By performing the first exposing step, the adhesion of the dry film **13** to the substrate **11** is increased and the dry film **13** remains on the substrate **11** side even when the support **14** is peeled off. Since pattern exposure is performed in the second exposing step without using the support **14**, according to the present embodiment, even when the foreign matter **18** is present on the support **14**, it is possible to suppress poor pattern formation caused by the foreign matter **18**.

Second Embodiment

In the manufacturing method illustrated in the first embodiment, the entire surface of the dry film **13** which is the first photosensitive layer is exposed via the support **14** which is the first support in the first exposing step. However, in the present disclosure, it is also possible to use a photomask **26** in the first exposing step to shield a predetermined region including the first region and the periphery in the dry film **13**. In a second embodiment, a photomask is used in the first exposing step and the dry film **13** is exposed while shielding the first region and the peripheral region of the dry film **13** to form the same structure **10** as that formed in the first embodiment. FIGS. **2**A to **2**H are diagrams illustrating the manufacturing process in the second embodiment. FIG. **2**A is a plan view of the structure **10** to be formed on the substrate **11** and in this drawing, the position of a light-shielding portion **27** in the photomask **26** in the first exposing step is illustrated by a broken line. FIGS. **2**B to **2**H are cross-sectional views taken along line A-A of FIG. **2**A and illustrate a manufacturing process in the present embodiment step by step corresponding to FIGS. **1**B to **1**H in the first embodiment, respectively.

FIG. **2**B illustrates a cross section of the substrate **11** and FIG. **2**C illustrates a dry film **13** formed on the support **14** prepared separately from the substrate **11**. As the substrate **11**, the dry film **13** and the support **14**, the same ones as those described in the first embodiment are used. As illustrated in FIG. **2**D, the dry film **13** is attached to and bonded to the substrate **11** via the support **14** so that the dry film **13** is in contact with one surface of the substrate **11**. This bonding is also performed in the same manner as in the first embodiment. Subsequently, as illustrated in FIG. **2**E, a first exposing step of exposing the dry film **13** via the support **14** is

performed. The first exposing step itself is performed in the same manner as in the first embodiment and in the second embodiment, the photomask **26** is disposed between a light source and the support **14** and the light **15** for exposure from the light source is shielded by the light-shielding portion **27** formed on the photomask **26**. The substrate **11** is provided with four openings **12** and for each opening **12**, a region including the opening **12** and the periphery is designated as a first region in the dry film **13**. The light-shielding portion **27** is formed in the photomask **26** slightly larger than the first region for each first region and a predetermined region including the first region and the periphery is not irradiated with the light **15**. Also in the present embodiment, the exposure amount in the first exposing step is an exposure amount that can cure the exposed region of the dry film **13** and is less than the resolution limit minimum exposure amount E_{th} of the dry film **13**.

Subsequently, as illustrated in FIG. **2**F, the support **14** is removed from the substrate **11** by peeling the support **14** from the dry film **13**. Since the portion exposed in the first exposing step, that is, a considerable portion of the second region is cured, it is possible to remove the first region in the developing step while preventing the dry film **13** from peeling from the substrate **11** when the support **14** is removed. Thereafter, the second exposing step is performed as illustrated in FIG. **2**G and further, the developing step is performed as illustrated in FIG. **2**H. The second exposing step and the developing step are performed in the same manner as in the case of the first embodiment. According to the present embodiment, even when the foreign matter is present on the support **14**, the second exposing step makes it possible to suppress a pattern formation defect caused by the foreign matter in the same manner as in the case of the first embodiment.

FIG. **3** is a diagram illustrating a manufacturing method for the structure **10** in a modification example of the second embodiment and illustrates the structure **10** formed on the substrate **11**. The difference from those illustrated in FIGS. **2**A to **2**H is the shape of the light-shielding portion **27** formed on the photomask **26** used in the first exposing step. In those illustrated in FIGS. **2**A to **2**H, a total of four light-shielding portions **27** are provided for each opening **12** of the substrate **11** and in this modification example, the photomask **26** is provided with a single light-shielding portion **27** in a shape that connects a plurality of openings **12** in the substrate **11**. In other words, a single predetermined region including a plurality of first regions set on the dry film **13** is shielded from light. Also in this case, when the exposure amount to the first region in the first exposing step is an exposure amount that can cure the dry film **13** and is less than the resolution limit minimum exposure amount E_{th}, it is possible to prevent the dry film **13** from peeling from the substrate **11** when the support **14** is removed. In addition, in this modification example, since the first exposing step only requires exposure with a rough pattern and dimension including the plurality of first regions, the degree of freedom of the process in the first exposing step can be increased.

Third Embodiment

Next, as a third embodiment, an example in which the manufacturing method for the structure according to the first embodiment is applied to the manufacture of a liquid ejection head will be described. The liquid ejection head is used in a liquid ejection device such as an ink jet recording device that ejects a liquid such as a recording liquid (for example, ink) to a recording medium and is a member that actually ejects the liquid from an ejection orifice in response to an applied signal. Before describing the manufacturing method for the liquid ejection head, a structure of the liquid ejection head will be described. FIG. **4** is a partially broken perspective view illustrating the configuration of a liquid ejection head **40**.

The liquid ejection head **40** includes the substrate **41** and an ejection orifice forming member **42**. The substrate **41** is made of, for example, single crystal silicon. Example of single crystal silicon include a silicon wafer having a crystal plane index of (**100**). On one surface of the substrate **41**, a plurality of energy generating elements **43** for generating energy used for ejecting the liquid is formed at predetermined intervals. As the energy generating element **43**, one of an electrothermal conversion element and a piezoelectric element is used. In a case where the energy generating element **43** is the electrothermal conversion element, ejection energy is generated when the energy generating element **43** heats a liquid in the vicinity thereof and causes a state change with respect to the liquid, for example, a state change from a liquid phase to a gas phase. A protective film (not illustrated) may be formed on the energy generating element **43** for protection. An electrode **44** connected to the energy generating element **43** by an electric wiring (not illustrated) is formed on one surface of the substrate **41** and the energy generating element **43** is driven by the electric power supplied from the outside of the substrate **41** via the electrodes **44**. Furthermore, the substrate **41** is formed with a liquid supply path **45** used for supplying the liquid to be ejected so as to penetrate between both surfaces thereof. A protective film (not illustrated) resistant to the liquid may be formed on the surface of the substrate **41** that comes into contact with the liquid.

The ejection orifice forming member **42** is made of, for example, a material such as resin and is provided on one surface of the substrate **41** so as to form at least a flow path **47** between the ejection orifice forming member **42** and the substrate **41** in a formation region of the energy generating element **43** on the substrate **41**. In the illustrated example, a pressure chamber **48** is also provided in addition to the flow path **47**. An adhesion layer (not illustrated in FIG. **4**) for improving these adhesions may be formed between the substrate **41** and the ejection orifice forming member **42**. In addition, in the ejection orifice forming member **42**, an ejection orifice **46** is formed as a through-hole for each energy generating element **43** of the substrate **41** so as to face the energy generating element **43**. The pressure chamber **48** is a space formed for each energy generating element **43** so that the energy generating element **43** is disposed on the bottom surface thereof and the ejection orifice **46** is disposed on the upper surface thereof and communicates with the liquid supply path **45** via the flow path **47**. The liquid supplied through the liquid supply path **45** is supplied to the pressure chamber **48** via the flow path **47** and is ejected from the ejection orifice **46** by the energy generated by driving the energy generating element **43**. In the configuration in which the pressure chamber **48** is not provided, the energy generating element **43** is provided on the bottom surface of the flow path **47**. In the present embodiment, the ejection orifice forming member **42** has a configuration in which a first layer **42**A forming a side wall portion of the flow path **47** and the pressure chamber **48** and a plate-shaped second layer **42**B on which the ejection orifice **46** is formed are laminated.

FIGS. **5**A to **5**L are cross-sectional views taken along line B-B of FIG. **4** and illustrate a manufacturing process of the liquid ejection head **40** illustrated in FIG. **4** step by step. As

described above and as illustrated in FIG. **5**A, the liquid supply path **45** is formed on the substrate **41** and the energy generating element **43** is formed in advance on one surface of the substrate **41**. Examples of the forming method for the liquid supply path **45** include dry etching such as reactive ion etching, laser ablation and processing by sandblasting. In a case where the substrate **41** is made of single crystal silicon, the liquid supply path **45** can be formed by wet etching using one of an aqueous solution of tetramethylammonium hydroxide (TMAH) and an aqueous solution of potassium hydroxide (KOH). The planar shape of the liquid supply path **45** is, for example, one of a circle and a quadrangular shape. In the example illustrated in FIG. **4**, the liquid supply path **45** has an elongated rectangular planar shape. The angle formed by the side wall of the liquid supply path **45** and one surface of the substrate **41** may be vertical and the liquid supply path **45** may have a tapered cross-sectional shape. A protective film (not illustrated) may be formed on one of each surface of the substrate **41** and the side wall of the liquid supply path **45**. The present invention is not limited to the forming method and shape of the liquid supply path **45**.

As illustrated in FIG. **5**B, a dry film **54** formed on a support **55**, which is a first support, is prepared separately from the substrate **41**. The dry film **54**, which is a first photosensitive layer, serves as an adhesion layer for improving the adhesion between the substrate **41** and the ejection orifice forming member **42** in the liquid ejection head **40**. The dry film **54** is, for example, a negative photosensitive resin and can be made of the material described with reference to FIG. **1**C in the first embodiment as an example. The thickness of the dry film **54** is, for example, in the range of 0.5 to 3 μm. As the support **55**, for example, a support made of one of a film, a glass substrate and a silicon substrate is used and in consideration of the ease of peeling off the support **55** after the dry film **54** is transferred to the substrate **41**, a film can be used. As an example, the material described with reference to FIG. **1**C in the first embodiment can be used for the support **55**.

Next, as illustrated in FIG. **5**C, the dry film **54** is attached to and bonded to the substrate **41** via the support **55** so that the dry film **54** is in contact with one surface of the substrate **41**. The dry film **54** is transferred and laminated on the substrate **41** by a laminating method while, for example, temperature and pressure are applied via the support **55**. In the implementation of the laminating method, for example, a roll-type transfer under vacuum can be performed in consideration of the discharge property of bubbles so that bubbles do not enter between the substrate **41** and the dry film **54**. In order to improve the adhesion between the substrate **41** and the dry film **54**, one surface of the substrate **41** may be treated with a silane material in advance.

Next, as illustrated in FIG. **5**D, a first exposing step of exposing the dry film **54** via the support **55** is performed. The type of light **56** used for exposure is not particularly limited as long as the light can expose the dry film **54** and transmits through the support **55** and ultraviolet rays can be used. The dry film **54** is divided into a first region in which the substrate **41** is exposed at the liquid supply path **45** and around the liquid supply path **45** by the developing step illustrated in FIG. **5**G and a second region, which is a region left on the substrate **41** in the developing step. In the first exposing step, it is necessary to expose the dry film **54** with an exposure amount that can cure the dry film **54** in order to improve the adhesion to the substrate **41** and the first region of the dry film **54** is a portion finally removed by development. Therefore, in a case where the first exposing step is performed by full exposure, the exposure amount can be less than the resolution limit minimum exposure amount E_{th} of the dry film **54**. The first exposing step may be performed by full exposure and may be performed by exposure in which a predetermined region including the first region is shielded by a photomask as in the second embodiment described above. Furthermore, the first exposing step may be performed by exposure in which a predetermined region including a plurality of first regions is shielded by a photomask having a single light-shielding portion, as in the modification example of the second embodiment.

Next, as illustrated in FIG. **5**E, the support **55** is removed from the substrate **41** by peeling the support **55** from the dry film **54**. Since the dry film **54** is cured by the first exposing step and the adhesion to the substrate **41** is improved, it is possible to prevent the dry film **54** from peeling off from the substrate **41** when the support **55** is removed. It is more desirable that the dry film **54** is tented on the liquid supply path **45** after the support **55** is removed. However, since the first region is a region removed in a later developing step, the dry film **54** at the position of the liquid supply path **45** may remain on the side of the support **55**. Before removing the support **55**, the dry film **54** may be heat-treated using, for example, a hot plate.

Next, as illustrated in FIG. **5**F, a second exposing step is performed. In the second exposing step, the first region of the dry film **54** is shielded by a light-shielding portion **58** of a photomask **57** and irradiated with light **56** to perform pattern exposure. In a case where there is an unexposed portion shielded by the foreign matter on the support **55** in the first exposing step, this unexposed portion is also exposed by the second exposing step. It is desirable that the exposure amount in the second exposing step is an exposure amount that allows the second region to be left in the developing step, that is, an exposure amount equal to or more than the minimum exposure amount of the dry film **54**. By this second exposing step, as described in the first embodiment, it is possible to suppress a pattern defect of the dry film **54** caused by the foreign matter on the support **55**.

Next, a developing step is performed to develop the dry film **54** and remove the first region of the dry film **54**. As a result, as illustrated in FIG. **5**G, a second region of the dry film **54** is formed on the substrate **41**. In particular, in the present embodiment, the dry film **54** is removed not only from the liquid supply path **45** but also from the position where the energy generating element **43** is formed on one surface of the substrate **41**. The developing step itself is performed in the same manner as that described with reference to FIG. **1**H in the first embodiment. In the same manner as in the case of the first embodiment, the heat treatment may be performed before the development and the heat treatment may be performed after the developing step.

Next, a dry film **59**, which is a second photosensitive layer, is prepared in the same manner as illustrated in FIG. **5**B and as illustrated in FIG. **5**H, the dry film **59** is laminated and bonded to one surface of the substrate **41**. This bonding is performed in a manner similar to that described with reference to FIG. **5**C. The dry film **59** is a portion of the ejection orifice forming member **42**, particularly a first portion **42**A (refer to FIG. **4**). The thickness of the dry film **59** is, for example, in the range of 5 to 25 μm, which corresponds to the height of the flow path **47** in the ejection orifice forming member **42**.

Next, as illustrated in FIG. **5**I, by photolithography using a photomask **60**, processing is performed to remove a flow path corresponding portion **62**, which is a portion corresponding to at least the flow path **47** in the ejection orifice

forming member **42**, from the dry film **59**. The exposing step here is a third exposing step and the flow path corresponding portion **62** is formed as a latent image. In the present embodiment, the flow path corresponding portion **62** also includes a portion corresponding to the pressure chamber **48**. In a case where the dry film **59** is a negative photosensitive resin, the portion irradiated with the light **56** remains as a pattern and the portion not irradiated with the light **56** is removed by development. Therefore, in the exposure at this time, the flow path corresponding portion **62** is prevented from being irradiated with the light **56** by the light-shielding portion **61** of the photomask **60**. In a case where the negative photosensitive resin used as the dry film **59** is of a chemically amplified type, after exposure via the photomask **60**, post exposure bake (PEB: post exposure/pre development bake) is performed before development. The dry film **59** may be developed at this stage. Alternatively, as will be described later, the latent image may be used to develop the dry film **59** together with the developing steps of other films to be laminated and exposed next. In the example illustrated here, the dry film **59** is developed together with the film laminated in the subsequent step. A high-precision alignment is performed by alignment marks (not illustrated) formed on the photomask **60** and the substrate **41**, respectively, by using photolithography. Therefore, the flow path **47** and the pressure chamber **48** can be accurately formed at desired positions with reference to the energy generating element **43**.

Next, a dry film **63**, which is a third photosensitive layer, is prepared in the same manner as that illustrated in FIG. **5**B, as illustrated in FIG. **5**J, the dry film **63** is laminated on the dry film **59** and a water repellent material (not illustrated) is further laminated on the dry film **63**. In laminating the dry film **63**, a method similar to that described with reference to FIG. **5**C can be used. The dry film **63** is a portion of the ejection orifice forming member **42**, particularly a second portion **42**B (refer to FIG. **4**). The thickness of the dry film is, for example, in the range of 3 to 7 μm, which corresponds to the thickness of the ejection orifice forming member **42** at the position of the ejection orifice **46** formed as a through-hole in the ejection orifice forming member **42**. The method of forming the water repellent material is selected according to the material. In a case where the water repellent material is made of, for example, a photosensitive resin composition, a film of the water repellent material may be formed by using, for example, one of a spin coating method and a slit coating method. The film thickness of the water repellent material is, for example, in the range of 0.1 μm to 1 μm. As the water repellent material, for example, an epoxy resin composition containing a fluorine-based water repellent component can be used and other materials can also be used.

Next, as illustrated in FIG. **5**K, by photolithography using a photomask **64**, processing is performed to remove an ejection orifice corresponding portion **66**, which is a portion corresponding to the ejection orifice **46** in the ejection orifice forming member **42**, from the dry film **63** and the water repellent material (not illustrated). For this processing, a method similar to that described with reference to FIG. **5**I can be used. The ejection orifice corresponding portion **66** is required to be connected to the flow path corresponding portion **62**. The exposing step here is a fourth exposing step and the ejection orifice corresponding portion **66** is formed as a latent image. The photomask **64** is provided with a light-shielding portion **65** corresponding to the position of the ejection orifice **46** on the ejection orifice forming member **42**. When both the dry film and the water repellent material (not illustrated) are of the chemically amplified type, PEB can be performed.

After the end of the exposure illustrated in FIG. **5**K, the development treatment is performed and as illustrated in FIG. **5**L, the flow path corresponding portion **62** of the dry film **59** and the ejection orifice corresponding portion **66** of the dry film **63** and the water repellent material (not illustrated) are removed. In a case where the dry film **59**, the dry film **63** and the water repellent material (not illustrated) are all negative photosensitive resins, the flow path corresponding portion **62** and the ejection orifice corresponding portion **66** can be collectively removed by using the same developing solution as that described with reference to FIG. **1**H in the first embodiment. A portion obtained by removing the unexposed portion by development and removing the flow path corresponding portion **62** from the dry film **59** is the flow path **47** and the pressure chamber **48**. A portion obtained by removing the ejection orifice corresponding portion **66** from the dry film **63** and the water repellent material (not illustrated) is the ejection orifice **46**. A high-precision alignment is performed by alignment marks (not illustrated) formed on the photomask **64** and the substrate **41**, respectively, by using photolithography. Therefore, the ejection orifice **46** can be accurately formed at a desired position with reference to the energy generating element **43**. Since the flow path **47** and the pressure chamber **48** are already formed at desired positions with high accuracy with reference to the energy generating element **43**, according to the present embodiment, the position accuracy between the energy generating element **43**, the ejection orifice **46**, the flow path **47** and the pressure chamber **48** can be improved.

Through the above steps, a main part of the liquid ejection head **40** in which the liquid supplied from the liquid supply path **45** is ejected from the ejection orifice **46** through the flow path **47** and the pressure chamber **48** is completed. Normally, in the manufacture of the liquid ejection head **40**, a silicon wafer corresponding to a plurality of substrates **41** is used and the ejection orifice forming members **42** corresponding to a plurality of liquid ejection heads **40** are collectively formed on one surface of the silicon wafer. Therefore, when the main part of the liquid ejection head **40** is completed as described above, the main part is cut and separated by dicing to obtain a plurality of chips corresponding to one liquid ejection head **40**, respectively. After mounting the electric wiring that drives the energy generating element **43** in each chip, a chip tank member for liquid supply is bonded. As a result, the liquid ejection head **40** is finally completed.

According to the present embodiment, even when the foreign matter is present on the support **55** when the dry film **54** is exposed via the support **55**, it is possible to suppress the occurrence of a pattern formation defect caused by the foreign matter. Therefore, in the liquid ejection head **40** according to the present embodiment, the occurrence of the pattern defect in the adhesion layer provided between the substrate **41** and the ejection orifice forming member **42** is suppressed and high reliability in the adhesion between the substrate **41** and the ejection orifice forming member **42** can be obtained. In a case where the liquid ejection head is used in a field such as commercial printing, it is necessary to maintain stable recording quality even when the recording liquid is ejected on a large amount of recording media. Therefore, it is necessary to improve the adhesion of the ejection orifice forming member **42** to the substrate **41**. According to the present embodiment, it is possible to obtain

a liquid ejection head **40** that can be used with high reliability even in fields such as commercial printing.

Manufacturing Example 1

Hereinafter, an example in which the liquid ejection head **40** is manufactured based on the third embodiment will be described. First, as illustrated in FIG. **5**A, a substrate **41** having a thickness of 625 μm made of single crystal silicon in which a plurality of energy generating elements **43** such as a heat generating resistor was disposed was prepared. The liquid supply path **45** was formed in advance on the substrate **41**. As illustrated in FIG. **5**B, a PET film having a thickness of 100 μm was used as the support **55** and a dry film **54** containing an epoxy resin (including N-695), which was a negative photosensitive resin composition, was prepared on the surface of the support **55**. The film thickness of the dry film **54** was 1 μm. As illustrated in FIG. **5**C, the substrate **41** and the dry film **54** were attached to each other and laminated by a laminating method under vacuum under the conditions of a stage temperature of 50° C., a roller temperature of 50° C., a roller pressure of 0.2 MPa and a roller speed of 1 mm/s. A roll laminating device was used for laminating. After bonding by laminating, as illustrated in FIG. **5**D, a first exposing step was performed by exposing the entire surface of the dry film **54** via the support **55** with light **56** having a wavelength of 365 nm using an exposure machine. The exposure amount at this time was 1500 J/m^2. This exposure amount is less than the minimum exposure amount E_{th} of the dry film **54**. After the first exposing step was performed, PEB was performed at a temperature of 50° C. for 4 minutes.

Next, as illustrated in FIG. **5**E, the support **55** was removed from the substrate **41** at room temperature. At this time, the dry film **54** did not peel off from the substrate **41**. The dry film **54** was tented on the liquid supply path **45**. Thereafter, as illustrated in FIG. **5**F, a second exposing step was performed in which the dry film **54** was pattern-exposed with light **56** having a wavelength of 365 nm from the exposure machine via a photomask **57**. The exposure amount in the second exposing step was 4000 J/m^2. This exposure amount is an exposure amount that exceeds the minimum exposure amount E_{th} of the dry film **54**. After the second exposing step was performed, PEB was performed at a temperature of 90° C. for 4 minutes. After completion of PEB, as illustrated in FIG. **5**G, a developing step using PGMEA as a developing solution was performed. As a result, an adhesion layer made of a pattern of the dry film **54** was formed on the substrate **41**. As a result of evaluating the shape of the adhesion layer made of the pattern of the dry film **54**, a pattern defect believed to be derived from the foreign matter on the support **55** was not detected.

After the developing step was performed, as illustrated in FIG. **5**H, on the substrate **41** having the pattern of the dry film **54**, the dry film **59** to be the ejection orifice forming member **42** was laminated and bonded in the same manner as described with reference to FIGS. **5**B and **5**C. The dry film **59** was supported by a support (not illustrated) different from the support **55**, which was the first support. The film thickness of the dry film **59** was 15 μm. The bonding of the dry film **59** to the substrate **41** was performed by a laminating treatment under vacuum using a roll type laminating device and the conditions at this time were a stage temperature of 50° C., a roller temperature of 50° C., a roller pressure of 0.2 MPa and a roller speed of 5 mm/s. Thereafter, the support (not illustrated) was peeled off at room temperature in the same procedure as that described with reference to FIG. **5**E.

Next, as illustrated in FIG. **5**I, the dry film **59** was irradiated with light **56** having a wavelength of 365 nm from the exposure machine via the photomask **60** to perform pattern exposure. The exposure amount was 10000 J/m^2. After the pattern exposure was performed, PEB was performed at a temperature of 60° C. for 4 minutes and thus a latent image was formed so that the flow path corresponding portion **62**, which was an unexposed portion of the dry film **59**, was the flow path **47** and the pressure chamber **48** in the ejection orifice forming member **42**. After forming the latent image, as illustrated in FIG. **5**J, the dry film **63** and the water repellent material (not illustrated) were laminated on the dry film **59**. The dry film **63** was made of the same negative epoxy resin as the dry film **54** and was prepared on a support (not illustrated) in the same manner as the method illustrated in FIG. **5**B. The dry film **63** was laminated on the dry film **59** by a laminating treatment under vacuum using a roll laminating device and the conditions at that time were a stage temperature of 50° C., a roller temperature of 50° C., a roller pressure of 0.2 MPa and a roller speed of 5 mm/s. After laminating on the dry film **59**, the support (not illustrated) supporting the dry film **63** was peeled off at room temperature. The film thickness of the dry film **63** was 5 μm. The water repellent material (not illustrated) was an epoxy resin containing a fluorine-based water repellent component, was formed to a film thickness of 0.6 μm by a slit coating method and then baked at 50° C. for 5 minutes to form a layer of the water repellent material on the surface of the dry film **63**.

Next, as illustrated in FIG. **5**K, the dry film **63** and the water repellent material (not illustrated) were irradiated with light **56** having a wavelength of 365 nm from the exposure machine via the photomask **64** to perform pattern exposure. The exposure amount was 1000 J/m^2. After the pattern exposure was performed, PEB was performed at a temperature of 90° C. for 4 minutes and thus a latent image was formed so that the ejection orifice corresponding portion **66**, which was an unexposed portion of the dry film **63** and the water repellent material, was the ejection orifice **46** in the ejection orifice forming member **42**. Subsequently, PGMEA was used as a developing solution to perform development for removing the latent image portion and as illustrated in FIG. **5**L, the flow path corresponding portion **62** of the dry film **59**, the dry film **63** and the ejection orifice corresponding portion **66** of the water repellent material (not illustrated) were collectively removed. In this manner, the ejection orifice **46** of the ejection orifice forming member **42**, the flow path **47** and the pressure chamber **48** are formed. Thereafter, the heat treatment was performed at a temperature of 200° C. for one hour in a nitrogen atmosphere to cure the ejection orifice forming member **42** made of a negative photosensitive resin. Thereafter, dicing, mounting of the electric wiring and bonding of the chip tank member were performed as described above to complete the liquid ejection head **40**.

Manufacturing Example 2

The liquid ejection head **40** was manufactured by the same steps as those in Manufacturing Example 1 described with reference to FIGS. **5**A to **5**L. In Manufacturing Example 1, when the support **55** was removed from the substrate **41** after the first exposing step, the dry film **54** was tented on the liquid supply path **45** as illustrated in FIG. **5**E.

On the other hand, in Manufacturing Example 2, the dry film **54** on the liquid supply path **45** remained on the support **55** side (not illustrated). Since the first region of the dry film **54** at the position corresponding to the liquid supply path **45** is a region removed in the developing step illustrated in FIG. **5**G, the dry film **54** may remain on the support **55** side. As a result of actually evaluating the shape of the adhesion layer made of the pattern of the dry film **54** after the developing step was performed, no pattern defect believed to be derived from the foreign matter on the support **55** was detected even in Manufacturing Example 2. As described above, also in Manufacturing Example 2, the pattern defect in the adhesion layer between the substrate **41** and the ejection orifice forming member **42** is suppressed and it is possible to form the liquid ejection head **40** having high reliability in the adhesion between the substrate **41** and the ejection orifice forming member **42**.

Fourth Embodiment

Although the above-described first and second embodiments use the dry film which is a negative photosensitive resin, the present disclosure can also be performed by using a positive photosensitive resin. In a fourth embodiment, a case where a pattern is formed on the substrate **11** by using the dry film **23** which is a positive photosensitive resin to form a structure **21** having the same shape as the structure **10** of the first embodiment will be described. FIGS. **6**A to **6**H are views illustrating a manufacturing method for a structure according to the fourth embodiment and FIG. **6**A is a plan view of the structure **21** to be formed on the substrate **11**. The structure **21** is the same as that illustrated in FIG. **1**A, except that the dry film provided on one surface of the substrate **11** is a positive dry film **23**. FIGS. **6**B to **6**H are cross-sectional views taken along line A-A of FIG. **6**A and illustrate a manufacturing process in the present embodiment step by step.

FIG. **6**B illustrates the substrate **11** and the substrate **11** is the same as that illustrated in FIG. **1**B. As illustrated in FIG. **6**C, the dry film **23** formed on the support **14** which is the first support is prepared separately from the substrate **11**. As the support **14**, the one described in the first embodiment can be used and as the dry film **23**, one made of a positive photosensitive resin is used. The forming method for the dry film **23** on the support **14** is the same as that in the case of the first embodiment. In addition, similarly to the first embodiment, the dry film **23** is divided into a first region removed by the developing step and a second region left even after the developing step. As illustrated in FIG. **6**D, the dry film **23** is attached to and laminated on the substrate **11** via the support **14** so that the dry film **23** is in contact with one surface of the substrate **11**. The bonding by laminating is also performed in the same manner as in the case of the first embodiment. After bonding, as illustrated in FIG. **6**E, a first exposing step of exposing the entire surface of the dry film **23** via the support **14** is performed. The exposure amount in the first exposing step is such that at least the second region is exposed with an exposure amount less than the minimum exposure amount. Since the positive dry film **23** is used here, the minimum exposure amount is an exposure amount at which the dry film **23** is removed in the developing step when the exposure amount is equal to or more than the exposure amount thereof.

After the first exposing step is performed, the support **14** is removed from the substrate **11** as illustrated in FIG. **6**F. This removing step is also performed in the same manner as in the case of the first embodiment. At this time, the dry film **23** at the position of the opening **12** of the substrate **11** can be tented on the opening **12** and since this region is a region removed by the developing step, the dry film **23** may remain on the side of the support **14**. After removing the support **14**, a second exposing step is performed as illustrated in FIG. **6**G. In the second exposing step, pattern exposure is performed on the dry film **23** via a photomask **28**. Unlike the case of the first embodiment, the photomask **28** is formed with a light-shielding portion **29** so that the second region of the dry film **23** is not exposed to the light **15**. Thereafter, by performing the developing step, as illustrated in FIG. **6**H, the structure **21** having the second region of the dry film **23** is formed on the substrate **11**. According to the present embodiment, even when the foreign matter is present on the support **14**, the second exposing step makes it possible to suppress a pattern formation defect caused by the foreign matter in the same manner as in the case of the first embodiment.

Manufacturing Example 3

An example in which the structure **21** is actually manufactured based on the fourth embodiment will be described. As illustrated in FIG. **6**C, a PET film having a thickness of 100 μm is used as the support **14** and a dry film **23** using a positive photosensitive resin composition (trade name: PMER, manufactured by TOKYO OHKA KOGYO Co., Ltd.) was prepared on the support **14**. The film thickness of the dry film was 1 μm. The bonding between the dry film **23** and the substrate **11** illustrated in FIG. **6**D was performed by a laminating treatment under vacuum using a roll laminating device. In the first exposing step illustrated in FIG. **6**E, light **15** having a wavelength of 365 nm was exposed to the entire surface of the dry film **23** via the support **14** using an exposure machine. The exposure amount at this time was equal to or less than the minimum exposure amount of the dry film **23**. After the first exposing step was performed, PEB was performed and then, as illustrated in FIG. **6**F, the support **14** was removed from the substrate **11** at room temperature.

Next, a second exposing step illustrated in FIG. **6**G was performed. In the second exposing step, the dry film **23** was pattern-exposed with light **15** having a wavelength of 365 nm from the exposure machine via the photomask **28**. The exposure amount at this time was set to an exposure amount equal to or more than the minimum exposure amount of the dry film **23**. After the second exposing step was performed, PEB was performed, a developing step using an aqueous TMAH solution as a developing solution was further performed and as illustrated in FIG. **6**H, a structure **21** having the pattern of the dry film **23** was formed on the substrate **11**. As a result of inspecting the shape of the structure **21**, no pattern defect believed to be derived from the foreign matter on the support **14** was detected.

Fifth Embodiment

As a fifth embodiment, another example of a manufacturing method for the liquid ejection head **40** will be described. In the third embodiment, although development is performed twice for forming the liquid ejection head **40**, in the fifth embodiment, the liquid ejection head **40** is manufactured by one development. The liquid ejection head **40** to be manufactured here is the same as that illustrated in the third embodiment and the difference is that the cross-sectional shape of the liquid supply path **45** is tapered so that the opening on one surface of the substrate **41** is narrower

than the opening on the other surface. FIGS. 7A to 7I are cross-sectional views taken along line B-B of FIG. 4 and illustrate a manufacturing process of the liquid ejection head 40 in the present embodiment step by step.

First, as illustrated in FIG. 7A, a first photosensitive layer 32 is formed on a support 31 which is the first support. The first photosensitive layer 32 is a layer disposed to improve the adhesion between the substrate 41 and the ejection orifice forming member 42. Although the first photosensitive layer 32 is not particularly limited as long as the first photosensitive layer 32 is a photosensitive layer and in the present embodiment, a photoresist made of a negative photosensitive resin is used. The first photosensitive layer 32 has a softening point of approximately 40° C. to 120° C. and the same material as that in the first embodiment can be used. In addition, it is desirable that a silane coupling agent is internally added to the first photosensitive layer 32 in order to enhance the adhesion. The first photosensitive layer 32 can be formed on the surface of the support 31 in the same manner as that in the first embodiment. The first photosensitive layer 32 can be formed on the surface of the support 31 with a thickness of 0.5 to 2 μm. In order to form the first photosensitive layer 32 having this thickness, the viscosity of the solution of the first photosensitive layer 32 can be 3 to 20 centipoise (cP). As the solvent used for forming the solution of the first photosensitive layer 32, the solvent described in the first embodiment can be used.

As described later, since the first photosensitive layer 32 on the substrate 41 is exposed (patterned) via the support 31, one of a glass substrate and an optical film having high light transmission is can be used for the support 31. Examples of the optical film that can be used include those made of one of an olefin film and a PET film. In addition, in order to transfer the first photosensitive layer 32 onto the substrate 41 with high accuracy, the support 31 can be made of a material having low flexibility and can have a flexural rigidity higher than that of the substrate 41. Since the flexural rigidity depends on the thickness of the member, the thickness of the support 31 can be appropriately set according to the thickness of the substrate 41. In addition, in order to facilitate the peeling off the support 31 from the first photosensitive layer 32 in the subsequent step, the support 31 may be subjected to a mold release treatment. As a mold release treatment on the support 31, for example, a thin film to be a release film can be applied onto the support 31 to form the thin film. For the thin film to be the release film, for example, one of a highly water repellent silicone resin and a resin containing a fluorine compound can be used.

Next, as illustrated in FIG. 7B, the first photosensitive layer 32 formed on the support 31 is turned upside down and placed on the substrate 41 so that the first photosensitive layer 32 is in contact with one surface of the substrate 41. By placing the first photosensitive layer 32 on the substrate 41, the liquid supply path 45 is blocked by the first photosensitive layer 32. Next, the first photosensitive layer 32 is laminated and bonded to the substrate 41 by applying pressure to deform the first photosensitive layer 32 under temperature conditions exceeding the softening point of the first photosensitive layer 32. Examples of the method of bonding the first photosensitive layer 32 to the substrate 41 include a laminating method and a pressing method. The substrate 41 is made of silicon, a liquid supply path 45 penetrating in the thickness direction thereof is formed in advance by silicon etching and an energy generating element 43 and a driving circuit (not illustrated) thereof are formed in advance on one surface of the substrate 41. The liquid supply path 45 is formed by forming a mask resist having an opening pattern of the liquid supply path 45 on the substrate 41 on which the energy generating element 43 is already formed and performing wet etching with one of an aqueous solution of TMAH and an aqueous solution of potassium hydroxide. Other etching methods include dry etching methods such as reactive ion etching (RIE). Examples of still another method of forming the liquid supply path 45 include a blasting method such as laser ablation and sandblasting. In a case where an electric heat converter is used as the energy generating element 43, a removable protective film may be attached to prevent the energy generating element 43 from being damaged when the liquid supply path 45 is formed on the substrate 41.

After the first photosensitive layer 32 is laminated and bonded to the substrate 41, as illustrated in FIG. 7C, as a first exposing step, the first photosensitive layer 32 is irradiated with light in the direction of the arrow via the support 31 and the photomask 36 to perform an exposure treatment. The photomask 36 is formed with a light transmitting portion illustrated in white blank in the drawing and a light-shielding portion illustrated in black. As a result of the exposure treatment, the first photosensitive layer 32 is formed with an unexposed portion 37 in which light is shielded by the photomask 36 and an exposed portion 38 irradiated with light. As described later, an adhesion layer 71 for improving the adhesion between the substrate 41 and the ejection orifice forming member 42 is formed from the exposed portion 38 of the first photosensitive layer 32.

Next, as illustrated in FIG. 7D, the support 31 is peeled off from the first photosensitive layer 32. As a method of peeling the support 31, there is a method of peeling while bending the support 31. In addition, in order to facilitate peeling off the support 31, a release film may be applied to the support 31 side before forming the first photosensitive layer 32. By peeling off the support 31, the first photosensitive layer 32 is bonded onto the substrate 41.

Subsequently, as illustrated in FIG. 7E, a second photosensitive layer 39 is placed and laminated on the first photosensitive layer 32. Although not illustrated here, the second photosensitive layer 39 is formed on a support different from the first support 31 and the second photosensitive layer 39 on the support is turned upside down and placed on the first photosensitive layer 32 formed on the substrate 41. The second photosensitive layer 39 is finally a member constituting at least a flow path 47 in the ejection orifice forming member 42, corresponding to the first layer 42A in the ejection orifice forming member 42. In addition, the second photosensitive layer 39 is also a member constituting the pressure chamber 48. Although the second photosensitive layer 39 is not particularly limited as long as the second photosensitive layer 39 is a photosensitive layer and in the present embodiment, a photoresist made of a negative photosensitive resin is used. The second photosensitive layer 39 has a softening point of approximately 60° C. to 120° C. and the material described in the first embodiment can be used as in the case of FIG. 7A. As a method of forming the second photosensitive layer 39 on a support (not illustrated), the method described in the first embodiment can be used as in the case of FIG. 7A. The second photosensitive layer 39 can be formed with a thickness of 3 to 25 μm. Examples of the laminating method for the second photosensitive layer 39 on the first photosensitive layer 32 include a laminating method and a pressing method. At the time of laminating, pressure can be applied to the second photosensitive layer 39 under a temperature condition exceeding the softening point of the second photosensitive layer 39. In the present embodiment, although the unex-

posed portion **37** and the exposed portion **38** are formed on the first photosensitive layer **32**, since the upper surface of the first photosensitive layer **32** is flat, the second photosensitive layer **39** can be stably placed and laminated on the first photosensitive layer **32**.

After the second photosensitive layer **39** is bonded on the first photosensitive layer **32**, as illustrated in FIG. **7**F, as a second exposing step, the second photosensitive layer **39** is irradiated with light in the direction of the arrow via the photomask **76** to perform an exposure treatment. The photomask **76** may have the same light-shielding portion pattern as that of the photomask **36** used in the first exposing step. The second photosensitive layer **39** can be a layer that is exposed to light having the same wavelength as that of the first photosensitive layer **32** and is, for example, photosensitive with a wavelength of 365 nm. The sensitivity of the second photosensitive layer **39** can be the same as or lower than the sensitivity of the first photosensitive layer **32**. As an example, the materials constituting the first photosensitive layer **32** and the second photosensitive layer **39** are determined so that the minimum exposure amount of the first photosensitive layer **32** is 0.5 when the minimum exposure amount of the second photosensitive layer **39** is 1. When the support (not illustrated) used to form the second photosensitive layer **39** is not peeled off and removed before the second exposing step is performed, the support is peeled off and removed after the second exposing step is performed. In the second exposing step, the unexposed portion **37** and the exposed portion **38** are also formed on the second photosensitive layer **39**. The unexposed portion **37** corresponds to a latent image formed on the second photosensitive layer **39** as a portion of the ejection orifice forming member **42** corresponding to at least the flow path **47**.

Subsequently, as illustrated in FIG. **7**G, the third photosensitive layer **70** is placed and laminated on the second photosensitive layer **39**. Although not illustrated here, the third photosensitive layer **70** is also formed on a support different from the support **31** which is the first support and the third photosensitive layer **70** on the support is turned upside down and placed on the second photosensitive layer **39**. Although not illustrated, a film having water repellency, that is, a water repellent film may be formed on the third photosensitive layer **70**. The water repellent film can be a film containing one of a silicon and fluorine-based water repellent component. The third photosensitive layer **70** is a plate-shaped portion of the ejection orifice forming member **42** on which the ejection orifice **46** is provided, that is, a second layer **42**B. Although the third photosensitive layer **70** is not particularly limited as long as the third photosensitive layer **70** is a photosensitive layer and in the present embodiment, a photoresist made of a negative photosensitive resin is used. The third photosensitive layer **70** has a softening point of approximately 40° C. to 60° C. and the material described in the first embodiment can be used as in the case of FIG. **7**A. As a method of forming the third photosensitive layer **70** on a support (not illustrated), the method described in the first embodiment can be used as in the case of FIG. **7**A. The third photosensitive layer **70** can be formed with a thickness of 3 to 20 μm. Examples of the laminating method for the third photosensitive layer **70** on the second photosensitive layer **39** include a laminating method and a pressing method.

After the third photosensitive layer **70** is bonded on the second photosensitive layer **39**, as illustrated in FIG. **7**H, as a third exposing step, the third photosensitive layer **70** is irradiated with light in the direction of the arrow via the photomask **77** to perform an exposure treatment. The photomask **77** is provided with a light-shielding portion corresponding to the position where the ejection orifice **46** is formed in the ejection orifice forming member **42**. When the third photosensitive layer **70** is exposed, it is desired that the first photosensitive layer **32** and the second photosensitive layer **39** are not exposed to light. Therefore, the third photosensitive layer **70** can have a photosensitivity to a wavelength different from those of the first photosensitive layer **32** and the second photosensitive layer **39**. Alternatively, when the third photosensitive layer **70** is exposed at the same wavelength as those of the first photosensitive layer **32** and the second photosensitive layer **39**, it is desired that the sensitivity of the third photosensitive layer **70** at the exposure wavelength is higher than the sensitivity of the first photosensitive layer **32** and the second photosensitive layer **39**. Here, high sensitivity means that the minimum exposure amount is small. As an example, the materials constituting the third photosensitive layer **70** is determined so that the minimum exposure amount of the third photosensitive layer **70** is 0.1 when the minimum exposure amount of the second photosensitive layer **39** is 1 at the exposure wavelength. By the third exposing step is performed, the unexposed portion **37** and the exposed portion **38** are also formed on the third photosensitive layer **70**. The unexposed portion **37** corresponds to a latent image formed on the third photosensitive layer **70** as a portion of the ejection orifice forming member **42** corresponding to at least the ejection orifice **46**. When the third exposing step is performed, the support (not illustrated) used for forming the third photosensitive layer **70** can be peeled off from the third photosensitive layer **70** before the exposure. In addition, after the support is peeled off, an additional exposure treatment may be performed using the photomasks **36** and **76** used in one of the first exposing step and the second exposing step. The reason for this is that since the third photosensitive layer **70** is the outermost layer, when a foreign matter is present on the support, the foreign matter may be an obstructive factor at the time of exposure and cause a pattern defect.

As illustrated in FIG. **7**I, the unexposed portion **37** in the photosensitive layers **32**, **39** and **70** is removed by performing a developing step of immersing the substrate **41** to which the photosensitive layers **32**, **39** and **70** are bonded in a developing solution after the third exposing step. As a result, an adhesion layer between the ejection orifice forming member **42** and the substrate **41** is formed from the first photosensitive layer **32**, the first layer **42**A of the ejection orifice forming member **42** is formed from the second photosensitive layer **39** and the second layer **42**B of the ejection orifice forming member **42** is formed from the third photosensitive layer **70**. In this developing step, the first photosensitive layer **32**, the second photosensitive layer **39** and the third photosensitive layer **70** are simultaneously developed at the same time. As the developing solution, the material described in the first embodiment can be used. In addition, after performing a developing treatment using a developing solution, a treatment of cleaning the substrate **41** with a rinsing solution may be performed. As the rinsing solution, one of isopropyl alcohol, ethanol and pure water can be used.

By going through each of the steps illustrated in FIGS. **7**A to **7**I, the main part of the liquid ejection head **40** in which the liquid supplied from the liquid supply path **45** as illustrated in FIG. **4** is ejected from the ejection orifice **46** through the flow path **47** and the pressure chamber **48** is completed. By mounting a member (not illustrated) for supplying the liquid to the liquid supply path **45** and an

electric wiring (not illustrated) for driving the energy generating element **43** on this main part, the liquid ejection head **40** is finally completed.

Here, with reference to FIGS. **8**A and **8**B, exposure in a case where a foreign matter **34** is present on the support **31** in the first exposing step will be described. As illustrated in FIG. **8**A, when an opaque foreign matter **34** is present on the support **31**, the light transmitted through the photomask **36** in the first exposing step is shielded by the foreign matter **34**. As a result, an unexposed portion **37** is generated in the first photosensitive layer **32**. Thereafter, when development is performed, as illustrated in FIG. **8**B, an unintended loss occurs in the pattern. Therefore, in the present embodiment, the first exposing step of exposing the first photosensitive layer **32** via the first photomask **36** is performed and thereafter the support **31** is removed. The second photosensitive layer **39** is laminated on the first photosensitive layer **32** after the support **31** is removed and before the second exposing step is performed. In the second exposing step, the second photomask **76** is used to perform pattern exposure of the second photosensitive layer **39** and the first photosensitive layer **32** is also exposed via the second photosensitive layer **39**. As a result, the unexposed portion **37** generated by the foreign matter **34** in the first exposing step is also exposed. As a result, the generation of the unexposed portion formed by being shielded from light by the foreign matter **34** is suppressed, so that the pattern loss due to the foreign matter **34** is suppressed. That is, in this case, it can be said that the second exposing step is a step of exposing the first photosensitive layer **32** without using the first support **31** used for forming the first photosensitive layer **32**. Since the first photosensitive layer **32** has higher sensitivity than that of the second photosensitive layer **39**, the light passing through the second photosensitive layer **39** can sufficiently expose the first photosensitive layer **32**.

Manufacturing Example 4

An example in which the liquid ejection head **40** is actually manufactured based on a fifth embodiment will be described. A silicon substrate was used as the substrate **41**. In a step of providing the liquid supply path **45** on the substrate **41**, the liquid supply path **45** was formed on the substrate **41** by immersing the substrate **41** in an aqueous solution (etching solution) in which TMAH was diluted to 22% and the temperature was adjusted to 83° C. for 20 hours. As the support **31**, an optical film having a thickness of 100 μm was used. As illustrated in FIG. **7**A, the first photosensitive layer **32** is applied to the surface of the support **31** to a thickness of 1 μm by a spin coating method, dried in an oven at a temperature of 50° C. to prepare the first photosensitive layer **32** on the support **31**. As the first photosensitive layer **32**, an epoxy resin and a photoinitiator dissolved in a solvent (PGMEA) were used. The photoinitiator was an agent for initiating photopolymerization when pattern formation was performed using photolithography in the first exposing step and was sensitive to light having a wavelength of 365 nm.

Next, as illustrated in FIG. **7**B, the first photosensitive layer **32** held by the support **31** was bonded to the substrate **41** on which the liquid supply path **45** was formed by using a vacuum laminating method. At that time, in order to ensure the accuracy of the thickness of the first photosensitive layer **32** formed on the substrate **41**, the temperature and pressure were regulated according to the softening point of the material of the first photosensitive layer **32**. Specifically, the first photosensitive layer **32** was bonded to the substrate **41** by pressurizing under the conditions of a temperature of 50° C., a pressure of 0.4 MPa and a pressurizing time of 60 seconds so that the thickness of the first photosensitive layer **32** was 1 μm. Thereafter, as illustrated in FIG. **7**C, a first exposing step was performed. In the first exposing step, a photomask **36** was used to irradiate the first photosensitive layer **32** with light having a wavelength of 365 nm at an exposure amount of 5000 J/m^2 via the support **31** to perform pattern exposure. Next, PEB was performed at a temperature of 50° C. for 5 minutes and thereafter the support **31** was peeled off from the first photosensitive layer **32**.

Next, as illustrated in FIG. **7**E, the second photosensitive layer **39** was laminated on the first photosensitive layer **32** formed on the substrate **41**. The second photosensitive layer **39** is prepared by applying the layer to a support made of an optical film having a thickness of 100 μm to a thickness of 15 μm by a spin coating method and drying in an oven at 50° C. The laminating of the second photosensitive layer **39** on the first photosensitive layer **32** was performed by a vacuum laminating method in which the second photosensitive layer **39** was placed on the first photosensitive layer **32** together with the support so as to be in contact with the first photosensitive layer **32**. At that time, the temperature and pressure were regulated according to the softening point of the material of the first photosensitive layer **32** so as not to soften the first photosensitive layer **32** too much. Specifically, the second photosensitive layer **39** was bonded to the first photosensitive layer **32** under the conditions of a temperature of 70° C., a pressure of 0.4 MPa and a pressurizing time of 60 seconds. Next, as illustrated in FIG. **7**F, in the second exposing step, the photomask **76** was used, the second photosensitive layer **39** was irradiate with light having a wavelength of 365 nm at an exposure amount of 10000 J/m^2 to perform pattern exposure. Next, PEB was performed at a temperature of 50° C. for 5 minutes.

Next, as illustrated in FIG. **7**G, the third photosensitive layer **70** was laminated on the second photosensitive layer **39**. The third photosensitive layer **70** is prepared by applying the layer to a support made of an optical film having a thickness of 100 μm to a thickness of 10 μm by a spin coating method and drying in an oven at 50° C. The laminating of the third photosensitive layer **70** on the second photosensitive layer **39** was performed by a vacuum laminating method in which the third photosensitive layer **70** was placed on the second photosensitive layer **39** together with the support so as to be in contact with the second photosensitive layer **39**. For the bonding of the third photosensitive layer **70**, the same conditions as the bonding conditions of the first photosensitive layer **32** were used. Next, as illustrated in FIG. **7**H, in the third exposing step, a photomask **77** was used, the third photosensitive layer **70** was irradiate with light having a wavelength of 365 nm at an exposure amount of 1000 J/m^2 to perform pattern exposure. Next, PEB was performed at a temperature of 90° C. for 5 minutes. Next, development was performed using PGMEA as a developing solution using a single-wafer dip developing device. As a result, each of the unexposed portions **37** of the first photosensitive layer **32**, the second photosensitive layer **39** and the third photosensitive layer **70** is removed and the main part of the liquid ejection head **40** having the cross-sectional structure of FIG. **7**I was obtained.

Sixth Embodiment

The manufacturing method for the structure based on the present disclosure is not used only for manufacturing the liquid ejection head. When a recessed portion is formed on

the surface of the substrate, the recessed portion can also be used for manufacturing a structure having one of a shape that covers the recessed portion and a shape that straddles the recessed portion. FIGS. **9**A to **9**H are cross-sectional views illustrating a manufacturing process of a structure according to a sixth embodiment of the present disclosure step by step.

First, as illustrated in FIG. **9**A, a first photosensitive layer **82** is formed on a support **81**, which is the first support. As the support **81**, the same support as the support **31** in the fifth embodiment can be used. The first photosensitive layer **82** is a photoresist having photosensitivity, may be one of a positive and a negative and here, a positive photoresist is used. As a forming method for the first photosensitive layer **82** on the support **81**, the same method as that described in the fifth embodiment can be used.

Next, as illustrated in FIG. **9**B, the first photosensitive layer **82** formed on the support **81** is turned upside down and placed on the substrate **84** so that the first photosensitive layer **82** is in contact with one surface of the substrate **84**. For example, a groove-shaped recessed portion **97** is previously formed on one surface of the substrate **84**. The recessed portion **97** may be a through-hole penetrating the substrate **84**. The recessed portion **97** is closed by the first photosensitive layer **82**. Thereafter, the first photosensitive layer **82** is bonded to the substrate **84** by the same method as that in the fifth embodiment.

Next, as illustrated in FIG. **9**C, a first exposing step is performed. In the first exposing step, the first photosensitive layer **82** is irradiated with light in the direction of the arrow via the support **81** and a photomask **86** to perform an exposure treatment. As a result, the first photosensitive layer **82** is formed with an unexposed portion **87** in which light is shielded by a light-shielding portion of the photomask **86** and an exposed portion **88** irradiated with light. In the present embodiment, since a structure is formed in which the recessed portion **97** is covered or the recessed portion **97** is straddled by using the positive first photosensitive layer **82**, the unexposed portion **87** is formed corresponding to the position directly above the recessed portion **97** and the position surrounding the recessed portion **97** on the substrate **84**. The exposed portion **88** corresponds to the first region of the positive first photosensitive layer **82**. The unexposed portion **87** corresponds to the second region of the first photosensitive layer **82** and is formed as a region that at least partially covers the recessed portion **97**. In a case where a negative layer is used as the first photosensitive layer **82**, the placement of the transmitting portion and the light-shielding portion in the photomask **86** is required to be reversed from that illustrated in FIG. **9**C. Thereafter, as illustrated in FIG. **9**D, the support **81** is peeled off from the first photosensitive layer **82** and the support **81** is removed from the substrate **84**. The peeling off the support **81** from the first photosensitive layer **82** is performed in the same manner as that in the fifth embodiment.

Next, as illustrated in FIG. **9**E, a second photosensitive layer **89** is formed on a support **91**, which is the second support, separately from the steps illustrated in FIGS. **9**A to **9**D. As the support **91**, the same one as the support **31** in the fifth embodiment can be used. Since the exposure is not performed through the support **91**, the support **91** may be opaque to the exposure light. The second photosensitive layer **89** is not particularly limited as long as the second photosensitive layer **89** is a photosensitive layer and here, the same type of positive photoresist as that of the first photosensitive layer **82** is used. When the first photosensitive layer **82** is positive, the second photosensitive layer can also be positive and when the first photosensitive layer **82** is negative, the second photosensitive layer **89** can also be negative. The second photosensitive layer **89** can be photosensitive with light having the same wavelength as that of the first photosensitive layer **82** and has, for example, photosensitive with a wavelength of 365 nm. The sensitivity of the second photosensitive layer **89** can be the same as or lower than the sensitivity of the first photosensitive layer **82**.

Next, as illustrated in FIG. **9**F, the second photosensitive layer **89** formed on the support **91** is turned upside down and the second photosensitive layer **89** is placed on the first photosensitive layer **82** formed on the substrate **84** so that the second photosensitive layer **89** is in contact with the first photosensitive layer **82**. At this time, although the unexposed portion **87** and the exposed portion **88** are formed on the first photosensitive layer **82**, the upper surface of the first photosensitive layer **82** is flat, so that the second photosensitive layer **89** can be stably placed on the first photosensitive layer **82**. By applying pressure to the second photosensitive layer **89** under a temperature condition exceeding the softening point of the second photosensitive layer **89**, the second photosensitive layer **89** is laminated and bonded to the first photosensitive layer **82**. At that time, the temperature and pressure can be regulated according to the softening point of the material of the first photosensitive layer **82** so that the first photosensitive layer **82** formed on the substrate **84** does not soften too much. As described later, the support **91** can be peeled off from the second photosensitive layer **89** after the second photosensitive layer **89** is bonded to the first photosensitive layer **82**.

Next, as illustrated in FIG. **9**G, a second exposing step is performed. In the second exposing step, the second photosensitive layer **89** is exposed by being irradiated with light in the direction of the arrow via a photomask **92**. At this time, the light transmitted via the photomask **92** reaches the first photosensitive layer **82** located below the second photosensitive layer **89**, so that the first photosensitive layer **82** is also exposed to light. By exposing the first photosensitive layer **82** to light in the second exposing step, the exposure of the unexposed portion of the first photosensitive layer **82** due to the foreign matter existing on the support **81** during the first exposing step is complemented in the second exposing step. As a result, according to the present embodiment, it is possible to prevent the occurrence of a pattern defect in the first photosensitive layer **82** due to the foreign matter on the support **81**. In addition, the second photosensitive layer **89** is the outermost layer in the structure of the present embodiment and when a foreign matter is present on the support **91** that supports the second photosensitive layer **89**, the foreign matter may be an obstructive factor at the time of exposure and causes a pattern defect. Therefore, the support **91** can be peeled off from the second photosensitive layer **89** before starting the second exposing step. In addition, after the support **91** is peeled off, an additional exposure treatment may be performed via the photomask **86** used in the first exposing step before the second exposing step is performed. As the photomask **92** used in the second exposing step, the photomask **86** used in the first exposing step may be used as it is. Furthermore, after the exposure using the photomask **92** is performed as the second exposing step, the additional exposure treatment may be performed using the photomask **86** used in the first exposing step.

Next, development is performed as illustrated in FIG. **9**H. In the developing step, the exposed portion **88** of the first photosensitive layer **82** on the substrate **84** and the exposed portion **88** of the second photosensitive layer **89** are dissolved in the developing solution and simultaneously removed and a structure in which the first photosensitive

layer **82** and the second photosensitive layer **89** are patterned on the recessed portion **97** of the substrate **84** is completed. After the developing step with the developing solution, a substrate cleaning treatment using a rinsing solution may be performed. Also in the present embodiment, even when exposure inhibition occurs in the first photosensitive layer **82** due to an exposure inhibitor such as a foreign matter on the support **81** during the first exposing step, since the portion where the exposure is hindered can be eliminated by the second exposing step, the occurrence of a pattern defect can be suppressed.

Manufacturing Example 5

Next, an example in which the structure is actually manufactured based on the sixth embodiment will be described. A silicon substrate was used as the substrate **84**. As the first photosensitive layer **82**, a positive photoresist containing silicon (Si) having etching resistance was used and a first photosensitive layer **82** having a thickness of 1 μm was formed on the support **81** in the same manner as that in the fifth embodiment. When the first photosensitive layer **82** was bonded to the substrate **84**, the first photosensitive layer **82** was bonded to the substrate **84** by laminating under vacuum under the conditions of a temperature of 90° C., a pressure of 0.4 MPa and a pressurizing time of 60 seconds so that the thickness of the first photosensitive layer **82** was 1 μm. Next, a first exposing step was performed. In the first exposing step, a photomask **86** was used to irradiate the first photosensitive layer **82** with light having a wavelength of 365 nm at an exposure amount of 5000 J/m^2 via the support **81** to perform pattern exposure. Next, PEB was performed at a temperature of 50° C. for 5 minutes and thereafter the support **81** was peeled off from the first photosensitive layer **82**.

As the second photosensitive layer **89**, a positive photoresist having etching resistance was used and a positive photoresist having an etching resistance was formed on the support **91** in the same manner as that in the fifth embodiment to a thickness of 5 μm. Next, the second photosensitive layer **89** held by the support **91** was laminated on the first photosensitive layer **82** formed on the substrate **84** by using a laminating method under vacuum. At that time, the temperature and pressure were regulated according to the softening point of the material of the first photosensitive layer **82** so that the first photosensitive layer **82** formed on the substrate **84** did not soften too much. The second photosensitive layer **89** was bonded to the first photosensitive layer **82** under the conditions of a temperature of 70° C., a pressure of 0.4 MPa and a pressurizing time of 60 seconds. After the support **91** was peeled off, a second exposing step was performed under the same conditions as the first exposing step, then PEB was performed and then a developing step was performed. In the developing step, an alkaline aqueous solution containing approximately 2.3% by mass of TMAH was used as the developing solution. After development, the substrate **84** was washed with pure water as a rinsing solution to complete the structure.

Hereinbefore, the embodiments of the present disclosure is described. The manufacturing method for the structure based on the present disclosure can be used, for example, for manufacturing the liquid ejection head. The liquid ejection head manufactured in this manner can be mounted on a device such as a printer, a copier, a facsimile having a communication system and a word processor having a printer unit and an industrial recording device combined with various processing devices. By using the device equipped with this liquid ejection head, recording can be performed on various recorded objects such as paper, thread, fiber, leather, metal, plastic, glass, wood and ceramic. In particular, the liquid ejection head manufactured based on the present disclosure is suitable for an ink jet recording head using a water-based ink. Furthermore, the present disclosure can also be applied to a manufacturing method for a liquid ejection head that ejects a liquid other than ink, for example, a liquid ejection head used for applications such as biochip manufacturing and electronic circuit printing. Furthermore, the present disclosure can be applied to a manufacturing method for a structure by patterning a photoresist which is a photosensitive resin composition on one of a substrate having no through-holes and a substrate having through-holes.

While the present disclosure has been described with reference to exemplary embodiments, it is to be understood that the invention is not limited to the disclosed exemplary embodiments. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

This application claims the benefit of Japanese Patent Application No. 2020-054241, filed Mar. 25, 2020, which is hereby incorporated by reference herein in its entirety.

What is claimed is:

1. A manufacturing method for a structure, comprising:

preparing a first photosensitive layer on one surface of a first support;

bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;

performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;

removing the first support after the first exposure;

performing a second exposure of the first photosensitive layer after the first support is removed via a photomask; and

developing the first photosensitive layer after the first exposure and the second exposure,

wherein

the first photosensitive layer is made of a negative photosensitive resin and is divided into a first region removed by the developing and a second region left after the developing,

in the first exposure, at least the first region is exposed with an exposure amount less than a minimum exposure amount of the first photosensitive layer,

in the second exposure, the second region is exposed with an exposure amount equal to or more than the minimum exposure amount of the first photosensitive layer, and

in the first exposure, a predetermined region of the first photosensitive layer including the first region is shielded and exposure is performed.

2. A manufacturing method for a structure, comprising:

preparing a first photosensitive layer on one surface of a first support;

bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;

performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;

removing the first support after the first exposure;

performing a second exposure of the first photosensitive layer after the first support is removed via a photomask; and

developing the first photosensitive layer after the first exposure and the second exposure,
wherein
the first photosensitive layer is made of a negative photosensitive resin and is divided into a first region removed by the developing and a second region left after the developing,
in the first exposure, at least the first region is exposed with an exposure amount less than a minimum exposure amount of the first photosensitive layer,
in the second exposure, the second region is exposed with an exposure amount equal to or more than the minimum exposure amount of the first photosensitive layer,
and in the first exposure, the first photosensitive layer is exposed via a first photomask,
the method further comprises
laminating a second photosensitive layer on the first photosensitive layer after removing the first support and before performing the second exposure,
in the second exposure, a second photomask is used as the photomask, the second photosensitive layer is pattern-exposed and the first photosensitive layer is also exposed via the second photosensitive layer, and
in the developing, the first photosensitive layer and the second photosensitive layer are simultaneously developed.

3. A manufacturing method for a structure, comprising:
preparing a first photosensitive layer on one surface of a first support;
bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;
performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;
removing the first support after the first exposure;
performing a second exposure of the first photosensitive layer after the first support is removed via a photomask;
developing the first photosensitive layer after the first exposure and the second exposure; and
performing additional exposure using the first photomask after laminating the second photosensitive layer,
wherein
in the first exposure, an entire surface of the first photosensitive layer is exposed.

4. A manufacturing method for a structure, comprising:
preparing a first photosensitive layer on one surface of a first support;
bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;
performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;
removing the first support after the first exposure;
performing a second exposure of the first photosensitive layer after the first support is removed via a photomask; and
developing the first photosensitive layer after the first exposure and the second exposure,
wherein
in the first exposure, an entire surface of the first photosensitive layer is exposed, and
in the first exposure, a predetermined region of the first photosensitive layer including the first region is shielded and exposure is performed.

5. The manufacturing method for a structure according to claim **1**, wherein
in the first exposure, a predetermined region of the first photosensitive layer including a plurality of the first regions is shielded and exposed.

6. The manufacturing method for a structure according to claim **1**, wherein
a gap between an end portion of the predetermined region of the first photosensitive layer in the first exposure and an end portion of a region where the first photosensitive layer is shielded in the second exposure is larger than an amount of deviation in alignment between the first exposure and the second exposure.

7. The manufacturing method for a structure according to claim **1**, wherein
an opening is formed on the one surface of the substrate and the first region is a region including a formation region of the opening in the first photosensitive layer.

8. A manufacturing method for a structure, comprising:
preparing a first photosensitive layer on one surface of a first support;
bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;
performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;
removing the first support after the first exposure;
performing a second exposure of the first photosensitive layer after the first support is removed via a photomask; and
developing the first photosensitive layer after the first exposure and the second exposure,
wherein
in the first exposure, an entire surface of the first photosensitive layer is exposed, and
in the first exposure, the first photosensitive layer is exposed via a first photomask,
the method further comprises
laminating a second photosensitive layer on the first photosensitive layer after removing the first support and before performing the second exposure,
in the second exposure, a second photomask is used as the photomask, the second photosensitive layer is pattern-exposed and the first photosensitive layer is also exposed via the second photosensitive layer, and
in the developing, the first photosensitive layer and the second photosensitive layer are simultaneously developed.

9. A manufacturing method for a structure, comprising:
preparing a first photosensitive layer on one surface of a first support;
bonding the first photosensitive layer and one surface of a substrate so that the first photosensitive layer and the substrate are in contact with each other;
performing a first exposure of the first photosensitive layer bonded to the substrate via the first support;
removing the first support after the first exposure;
performing a second exposure of the first photosensitive layer after the first support is removed via a photomask;
developing the first photosensitive layer after the first exposure and the second exposure; and
performing additional exposure using the first photomask after laminating the second photosensitive layer,
wherein
the first photosensitive layer is made of a negative photosensitive resin and is divided into a first region removed by the developing and a second region left after the developing,

in the first exposure, at least the first region is exposed with an exposure amount less than a minimum exposure amount of the first photosensitive layer, and

in the second exposure, the second region is exposed with an exposure amount equal to or more than the minimum exposure amount of the first photosensitive layer.

10. The manufacturing method for a structure according to claim **2**, wherein

light having the same wavelength is used in the first exposure and the second exposure and the first photosensitive layer has higher sensitivity than that of the second photosensitive layer at the wavelength.

11. The manufacturing method for a structure according to claim **2**, wherein

an opening is formed on the one surface of the substrate and the first region is a region including a formation region of the opening in the first photosensitive layer.

12. The manufacturing method for a structure according to claim **2**, wherein

a recessed portion is formed on the one surface of the substrate and the second region is a region at least partially covering the recessed portion in the first photosensitive layer.

13. The manufacturing method for a structure according to claim **1**, wherein

the first photosensitive layer is made of a positive photosensitive resin and is divided into a first region removed by the developing and a second region left after the developing,

in the first exposure, at least the second region is exposed with an exposure amount less than a minimum exposure amount of the first photosensitive layer, and

in the second exposure, the first region is exposed with an exposure amount equal to or more than the minimum exposure amount of the first photosensitive layer.

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